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ABSTRACT

This technical specialty course is one of thirty-five courses designed for use by two-year postsecondary institutions in five nuclear technician curriculum areas: (1) radiation protection technician, (2) nuclear instrumentation and control technician, (3) nuclear materials processing technician, (4) nuclear quality-assurance/quality-control technician, and (5) nuclear reactor (plant) operator trainee. This course, Power Plant Chemistry, contains seven modules: Water Quality Control; Raw-Water Treatment; Sources of Impurities in Reactor Water Systems; Water Treatment: Polishing by Ion Exchange, Evaporation, and Demineralization; Water Properties Sensing; Water Analysis of Nuclear Power Plants; and Radioactive Waste Handling: Liquid and Gaseous. Each module follows a typical format including the following sections: introduction, module prerequisites, objectives, subject matter, exercises, materials, procedures, data tables, reference materials, and tests. (A master index and suggested program planning guides are also available--see CE 026 856 and CE 026 639-643.) (LRA)

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Nuclear Technology Series

COURSE 13
POWER PLANT CHEMISTRY

TECHNICAL EDUCATION RESEARCH CENTER - SW

4201 LAKE SHORE DRIVE - SUITE 111

WACO, TEXAS 76710

CE 026 654

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SEP 1980

PREFACE

ABOUT NUCLEAR TECHNOLOGY MODULES

The modules - developed by TERC-SW for use in two-year postsecondary technical institutions to prepare technicians for employment - are useful in industry for updating employees in company-sponsored training, and as laboratory texts in engineering schools. The principles, techniques and skills taught in the modules, based on tasks that nuclear technicians perform, were obtained from a nationwide advisory committee of employers of nuclear technicians. Each module was written by a working technical expert and tested with students.

A module contains the following elements:

Introduction, which identifies the topic and often includes a rationale for studying the material.

Module Prerequisites, which identify the material a student should be familiar with before studying the module.

Objectives, which clearly identify what the student is expected to know for satisfactory module completion. The objectives, stated in terms of action-oriented behaviors, include such action words as operate, measure, calculate, identify and define, rather than words with many interpretations, such as know, understand, learn and appreciate.

Subject Matter, which presents the background theory and techniques supportive to the objectives of the module. Subject matter is written with the technical student in mind.

Exercises, which provide practical problems to which the student can apply this new knowledge.

Materials, which identify the equipment required to complete the laboratory procedure.

Procedures, which is the experiment section, or "hands-on" portion of the module (including step-by-step instruction) designed to reinforce student learning.

Data Tables, which are included in most modules for the first year (or basic) courses to help the student learn how to collect and organize data.

Reference Materials, which are included as suggestions for supplementary reading/viewing for the student.

Test, which measures the student's achievement of the prestated objectives.

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The Nuclear Technology Series will consist of five curricula when completed:

Nuclear Reactor (Plant) Operator Trainee.
Radiation Protection Technician.
Nuclear Materials Processing Technician.
Nuclear Quality-Assurance/Quality-Control Technician.
Nuclear Instrumentation and Control Technician.

The completed Nuclear Reactor (Plant) Operator Trainee curriculum consists of the following sixteen technical specialty courses made up of 114 instructional modules:

Radiation Physics.
Radiation Protection I.
Principles of Process Instrumentation.
Heat Transfer and Fluid Flow.
Introduction to Nuclear Systems.
Instrumentation and Control of Reactors and Plant Systems.
Reactor Operations.
Reactor Safety.
Reactor Auxiliary Systems.
Power Plant Systems.
Radiation Detection and Measurement.
Reactor Physics.
Power Plant Chemistry.
Introduction to Quality Assurance/Quality Control.
Metallurgy and Metals Properties.
Mechanical Component Characteristics and Specifications.

Availability: Instructional modules are available individually or by courses from:

Technical Education Research Center - Southwest
4201 Lake Shore Dr., Suite 111
Waco, Texas 76710
Telephone (817) 772-8756

Printed:

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Module 13-6 Water Analysis for Nuclear Power Plants

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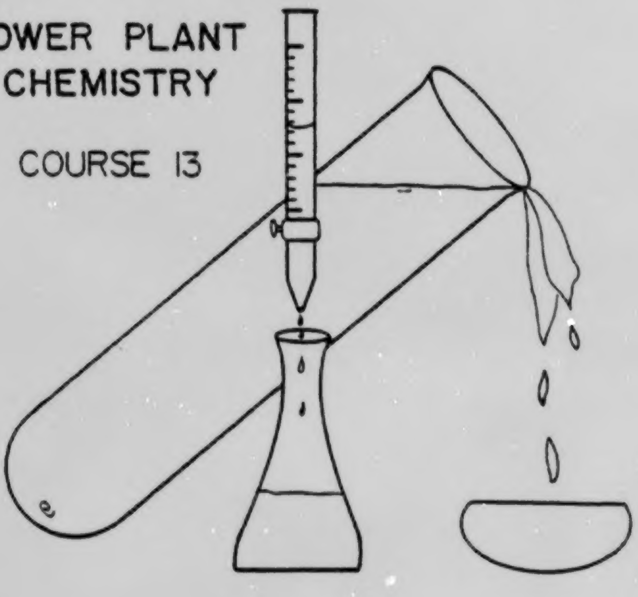
NUCLEAR TECHNOLOGY

MODULE 13-1 WATER QUALITY CONTROL. -

ROBERT B. NEEL

POWER PLANT CHEMISTRY

COURSE 13



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COURSE MODULES

COURSE 13 POWER PLANT CHEMISTRY

⇨ MODULE 13-1	Water Quality Control
MODULE 13-2	Raw-Water Treatment
MODULE 13-3	Sources of Impurities in Reactor Water Systems
MODULE 13-4	Water Treatment - Polishing by Ion Exchange, Evaporation and Demineralization
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INTRODUCTION

Nuclear power plant cooling systems utilize high purity water to minimize material corrosion. In a reactor cooling system, designed to recycle up to 15 million pounds of water an hour, a concentration of impurity of one part per billion (i.e., one pound of impurity in 1 billion pounds of solution) could result in as much as 150 pounds of corrosion products in a year. Before taking water from rivers, lakes or wells into the cooling systems of the plant, most of these impurities must be chemically or physically removed or reduced.

Dissolved impurities may become radioactive while in the reactor core region. If circulated into other parts of the plant, they may expose personnel to irradiation.

Certain impurities, which remain in solution, may lead to chemical corrosion of metals in valves, piping and other components of the plant including the reactor. Such corrision products also may precipitate out of the cooling water onto hot surfaces, producing reduced heat transfer capability and shortened life of heat exhangers.

This module idenitifes the most common impurities to be removed from cooling water. Also, it introduces the most common methods of removing these impurities, and of monitoring purified water to ensure that its purity remains at a high level.

MODULE PREREQUISITES

The student should have a basic course in algebra and general chemistry, plus Module 10-1 of Course 10, "Power Plant Fundamentals."

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Explain how the water impurities listed below could affect a plant cooling system:
    - Anionic impurities, including chloride, fluoride, hydroxide, carbonate and bicarbonate.
    - Gaseous impurities, such as oxygen and carbon dioxide.
    - Color impurities and certain living organisms, such as algae.
2. List typical values for total solids, dissolved oxygen, pH and conductivity in both PWR and BWR reactor cooling system water.
3. Describe types of make-up water treatment used in reactor cooling systems:
    - Clarification.
    - Softening.
    - Chloration.
    - Filtration.
    - De-areation.

Ion exchange.
Demineralization.

4. Explain how more common power plant instruments measure water properties; list four impurities and the instrument used to measure each.
5. Define:

    - ppb.
    - Hard water.
    - Surface water.
    - Make-up water.
    - Anion.
    - Turbidity.
    - Ground water.
    - Dissolved solids.
    - Suspended solids.
    - Total solids.
    - Cation.

SOURCES OF RAW WATER

Although over three-quarters of the surface of the earth is covered with water, the prime sources of raw (natural) water are presently restricted to fresh surface and ground waters.

SURFACE WATER

To collect surface water from a lake or river, a tower is placed near its shore to intake clean water, or water of a desired temperature or purity. These vertical structures are usually provided with inlets at different depths in the water to allow level selection for water removal. This water often contains such organic matter as leaf mold, and such insoluble matter as sand and silt. Frequently, pollution from industrial sewage also is present. The suspended matter in large lakes and reservoirs also can vary widely. On the other hand, soluble minerals, such as sodium chloride or (rare) calcium chloride, often show little variation.

GROUND WATER

Ground water is the most common source of public, as well as private, water in the United States. Ground water picks up impurities as it seeps down from the surfaces through rock strata, dissolving some part of almost every chemical it encounters.

RAW-WATER CONVERSION TO INDUSTRIAL WATER

Industrial practice normally describes impurity content of water in the following terms:

Dissolved solids.
Suspended solids.
Total solids.

Dissolved solids is a measure of the total amount of chemicals dissolved in water. It is determined by evaporation and by weighing the residue. A high concentration of dissolved solids is objectionable because it interferes with efficient heat-transfer processes and is a cause of foaming in boilers. Ionic solids (a form of dissolved solids) are positively charged cations and negatively charged anions formed by solid matter dissolved by ionization into water solutions. These solids, normally measured by electrical conductivity of the solution, can increase the corrosive character of water.

Suspended solids is a measure of undissolved chemicals. Usually determined by filtration followed by weighing of collected solids, these solids plug lines and cause deposits in heat exchangers, boilers and other equipment.

Total solids is the sum of dissolved and suspended solids. Both suspended and dissolved solids may deposit on the reactor core or other heat-exchanger surfaces to produce reduced heat transfer. Plugging of fluid flow paths in the reactor in the reactor and possible corrosion or pitting of reactor metals are other potential problems attributable to total solids.

COMMON RAW-WATER IMPURITIES

Suspended solids form a fraction of water impurities, including turbidity and living organisms. Turbidity refers to a suspension of insoluble clay and other mineral solubles of less than 50-micron (2×10^{-3} inches or 2 mils) diameter. That part of the turbidity that is less than 5 microns in diameter usually remains suspended in solution for weeks, months or years, and is called colloidal matter. A common example of turbid water is a muddy river.

Living organism masses can grow to proporations such that their deposits reduce pipe cross sections, inhibiting flow. Micro-organisms that occur in surface water include:

Diatoms.
Molds.
Bacterial slimes.
Algae - plant-like organism.

(Deep well water, because of the filtering action of soil, is usually free of such organisms.)

Common forms of dissolved solids in impure water include:

Salts of calcium.
Magnesium silica.
Materials giving color to the water.
Hard water (i.e., water containing primarily bicarbonate and sulfate salts of calcium and magnesium).

The principal deleterious effect of hardness is to leave solid deposits when water evaporates. These deposits can reduce the cross sections of pipes, clog valves and reduce flow rates of cooling water (Figure 13-1-1). The deposits also can decrease heat transfer.

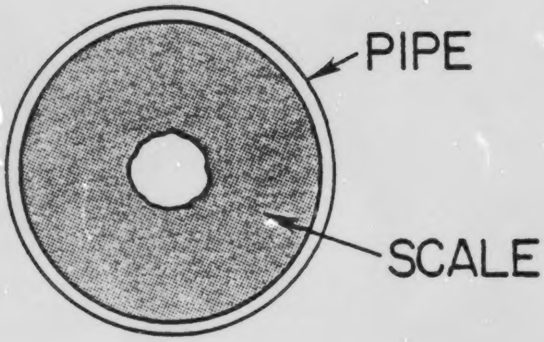

Figure 13-1-1.
Scale deposits reduce pipe cross section.

Silica, dissolved sodium silicate (Na_2SiO_3), forms insoluble deposits with calcium, magnesium or iron. Permissible concentrations of silica in a coolant system depend on system operating pressure - the higher the pressure, the lower the silica content allowed.

Several negatively charged ions are known to enhance corrosion of reactor metals. For example, the effect of chloride, hydroxide and fluoride ions on a water system is to enhance corrosion of some stainless steels at very low impurity concentrations, especially in the presence of heat or stress or dissolved oxygen. Fluoride ions have been shown to enhance corrosion of fuel-rod cladding (Zircaloy-4). Other steels crack in concentrated caustic solutions that contain hydroxide ions. The bicarbonate ion (HCO_3^-), if not removed, can react with steam (in the steam generator) to produce carbonic acid. Bicarbonate and hydroxide ions also can lead to foaming in a BWR or in the secondary of a PWR steam generator.

Gases dissolved in water include:

Oxygen.

Nitrogen.
Carbon dioxide.
Hydrogen sulfide.
Ammonia.

Hydrogen sulfide, an acid, has an odor of rotten eggs. Water containing this gas is as corrosive to most metals as it is distasteful.

Surface water generally contains less carbon dioxide than ground water; however, well water normally contains no more than 50 ppm carbon dioxide.

The most common gas dissolved in water is oxygen. It is very corrosive to reactor structural materials. The rapid corrosion of certain steels requires the presence of dissolved oxygen.

Ammonia (NH_3), sometimes present, can cause corrosion of zinc and copper alloys (for example, the copper inner tubes of certain condenser heat exchangers).

COMMON RAW-WATER TREATMENTS

Once an adequate supply of raw water is available, a decision must be made as to which of the possible water treatments to use. Since the types and concentrations of impurities are unique for each source of water, the water treatment system also may be unique. The methods presented for water treatments (in this module) merely illustrate the particular types that might be involved. The hypothetical water contains dissolved and suspended solids, color, odor, turbidity, hardness and dissolved gases.

The processes most commonly used to treat water include:

Clarification.
Filtration.
De-aeration.
Chlorination.
Lime-soda softening.

These treatments convert raw water to industrial water (Figure 13-1-2). A very brief discussion of each follows.

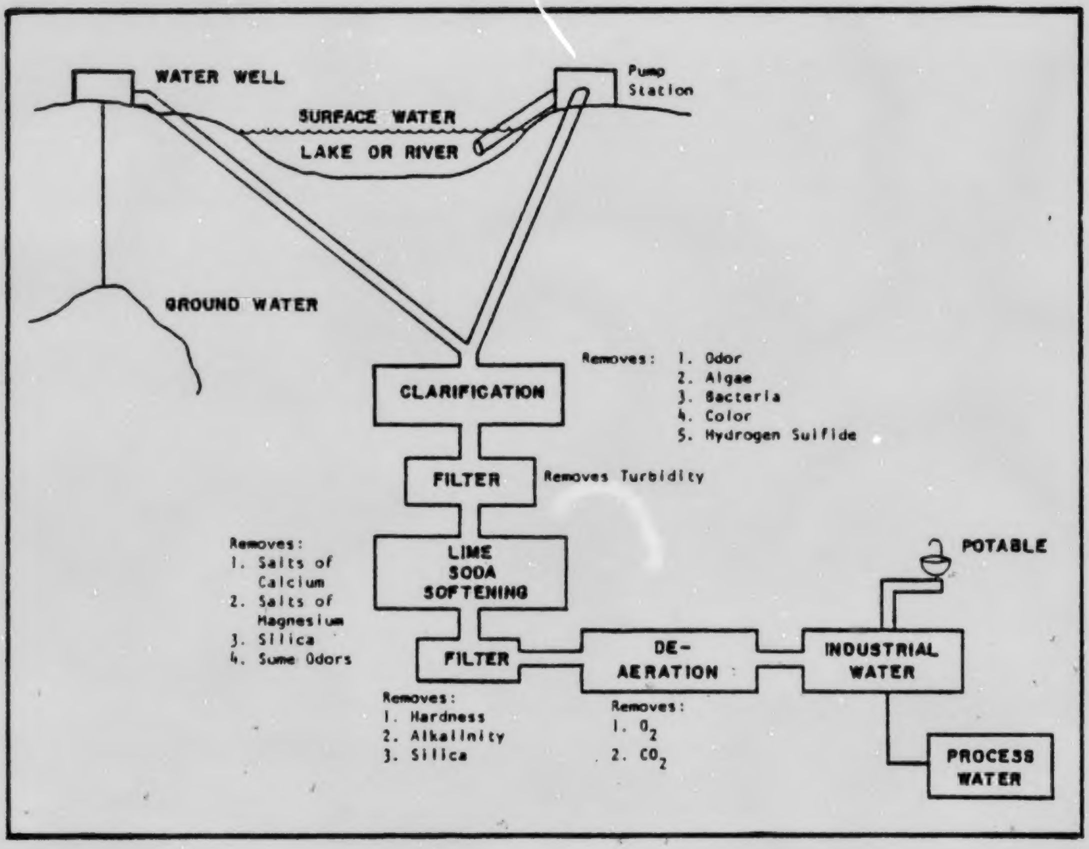

Figure 13-1-2. Conversion of raw water to industrial water.

Clarification processes cause colloidal particles to coalesce (form larger particles), which settle more rapidly. Coagulants, such as alum or ferris sulfate, produce gelatinous colloids that coat the impurity particles. This coating causes the impurity particles to adhere to each other in a floc (loose aggregate). The larger aggregates of floc settle into a basin and then are drawn off the clear fluid above the floc. The floc contains the turbid materials and most of the color. Chlorine gas may be introduced into this clarification system to remove odors, algae, slime and bacteria. Chlorine gas also reacts with the hydrogen sulfide dissolved in the water to aid in its removal.

Clarified water must be filtered to remove the floc, which contains the turbidity, color and suspended solids. In the most widely used filter, a rapid sand filter, filtration is vertically downward through a deep bed of sand.

Lime-soda softening commonly is applied to remove dissolved salts of calcium and magnesium, silica and other hardening solids. Lime (calcium hydroxide) and soda (sodium carbonate) are added to the water in fixed proportions. Calcium and magnesium ions are precipitated as calcium carbonate and magnesium carbonate, then removed as solid impurities. Dissolved carbon dioxide also may be removed with lime, as calcium carbonate. Silica in water reacts with added magnesium to produce insoluble magnesium silicate. This process may be carried out at ambient temperature or at elevated temperature, using steam to heat the liquids during precipitation. Precipitated sludge, which contains the hardness, the alkalinity and the silica, passes through a rapid sand filter.

Removal of undesirable gases and volatile impurities (for example: odor, ammonia, hydrogen sulfide, CO_2, volatile organic matter and oxygen) is accomplished best by deaeration (intermixing steam with gasified water). The resulting hot water, while undergoing violent agitation, loses the dissolved gases, which are subsequently vented to the atmosphere.

After this total process, the raw water is converted to industrial water usable as process water or, with slight modification, potable (drinking) water. Although the water appears clear at this point, and is not hard, it still is not adequate for use as circulating cooling water (for most reactors).

REACTOR MAKE-UP WATER PREPARATION

Industrial water still contains dissolved impurities that must be removed before it can be introduced into a reactor cooling system as make-up water. This make-up water should contain no more than negligible amounts of hardness, alkalinity and dissolved or suspended solids. Water treated by the lime-soda process must be treated further (it usually contains between 20 and 40 ppm of hardness and alkalinity as well as several hundred ppm of dissolved solids). Steps in the conversion of industrial water to reactor make-up water (Figure 13-1-3) are discussed below.

ION-EXCHANGE PROCESS

An ion-exchange process chemically removes dissolved impurities as well as mechanically removing some particulate matter. Ion exchangers contain organic materials formulated

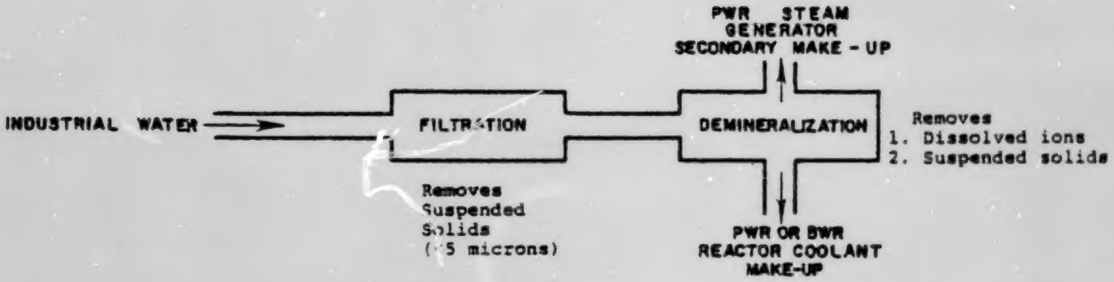

Figure 13-1-3. Industrial water conversion to reactor make-up water.

into resin beads a few millimeters in diameter. These resins are manufactured in two major forms:

Strong acid, which binds cations to itself.

Strong base, which binds anions to itself.

When a solution that contains strong cation and anion impurities is poured over a bed of either resin type, the impurity atoms replace or exchange with the more loosely bound hydroxide or hydrogen ions (that is, the bed appears to "absorb" the dissolved impurity ions). Eventually, the impurities, which have collected on the ion exchangers, fill up the collection removal sites, and must be replaced with new resins, or the old resins must be regenerated.

DEMINERALIZATION

Frequently, fixed proporations of both anions and cations (from ion-exchange resins) mix in a bed to form a demineralizer. This mixed-bed resin removes nearly all dissolved ions from the effluent, producing essentially deionized or demineralized water. When the turbidity of the raw water supply is less than 10 ppm, an ion exchanger can be used directly to remove dissolved solids without clarification or lime-soda softening. Because the beds of ion-exchange resins are several feet thick, they tend to mechanically remove some of the fine particles, i.e., those less than 1 micron in diameter, which remain as suspended solids after the lime-soda softening process. Commonly, cartridge filter units are used before and after demineralizers to trap small particles. (This filter is discussed in Module 13-4, "Water Treatment - Polishing by Ion Exchange, Evaporation & Demineralization.") After demineralization, make-up water can be used in a PWR steam generator or in reactor core cooling systems of either a PWR or a BWR.

Typical reactor make-up water qualities are given in Table 13-1-1.

TABLE 13-1-1
TYPICAL QUALITY FOR REACTOR MAKE-UP WATER

	PWR	BWR
Total solids	1.0 ppm	--
Dissolved oxygen	0.1 ppm	--
Chlorides	0.1 ppm	<0.05 ppm
Fluorides	0.1 ppm	--
pH at 77°F	6.5 - 7.5	6 - 8
Conductivity	< 1µmho/cm	< 1µmho/cm

REACTOR COOLANT PURIFICATION SYSTEM

Although a reactor coolant system (PWR or BWR) contains essentially pure water, corrosion products are still formed by remaining dissolved chemicals in the coolant. Dissolved gases, such as oxygen and carbon dioxide, promote corrosion of reactor metallic components (for example, valves, piping and pressure vessel) by forming metal oxides. Dissolved solids, such as sodium chloride, sodium hydroxide and fluorides, promote corrosion in metals, especially those under stress at high temperatures.

ACTIVATED CORROSION PRODUCTS

Corrosion products, circulating in reactor coolant, become radioactive by absorption of thermal neutrons from the core. These products (mostly oxides of iron, chromium or nickel - some soluble in the coolant) are commonly called "crud." They are trapped within the cooling system by rough, uneven surfaces, at times, hundreds of feet from their point of origin. Thus, it is possible for corrosion products, generated in the system, activated in the reactor core, redistributed throughout the system, to produce a radiation hazard to plant personnel.

Build-up of crud also reduces heat transfer from the fuel rods to the coolant.

FISSION PRODUCTS IN THE COOLANT

Fission products in the coolant originate from two sources:

Micro-cracking, which may occur in fuel rods that have been in operation for some time.

Trace uranium, particularly at the beginning of reactor life.

Though Zircaloy fuel cladding prevents gross leakage of fission gases into reactor coolant, small amounts occasionally escape through micro-cracks in the fuel cladding. These gases, usually products of uranium-235 fission, are mainly radioactive isotopes of iodine, xenon and krypton. Also, very small amounts of metallic ions (such as cesium) diffuse through the micro-cracks into the coolant, and these too must be removed.

Zircaloy normally contains trace amounts of uranium as an impurity - typically 1/10 ppm - particularly in welds. Fission fragments near the surface can be injected into the coolant with considerable energy.

Not only do circulating fission or corrosion products form deposits on reactor components, but droplets of reactor coolant may be carried over by steam (produced in a BWR) and evaporate on turbine parts. As they evaporate, dissolved ions plate onto the blades to form a type of boiler scale. Some of these dissolved elements, such as the silica, are volatile enough to be carried over and deposited on their own.

In a PWR steam generator, boiler scale also may be formed on boiler tubes as water evaporates on the shell side. Droplets of water containing dissolved corrosion products also can produce turbine deposits of thermally insulating solids.

REACTOR WATER POLISHING

For the reasons given above, reactor cooling water must be purified continously. This process, called "polishing," is accomplished by mechanical filters and demineralizers (e.g., mixed-bed ion exchangers).

Three general types of filters are used:

Cartridge.
Pre-coat.
Deep bed.

Cartridge filters vary in size and are relatively inexpensive to install. They remove circulating crud in sizes greater than 1-micron diameter. Frequently, they are used in conjunction with pre-coat filters, which remove crud particles of less than 1-micron diamter. Since a pre-coat filter system includes a pre-coat mixing tank, mixers, pumps and automatic valves, it is considerably more expensive than a cartridge filter system.

A deep-bed filter is used in the reactor purification system of a BWR or PWR. It is also used in those once-through steam generators marketed by The Babcock and Wilcox Company. The bed, several feet deep, contains cation and anion resins intimately mixed in proper proportions to effectively demineralize water. (It is, therefore, sometimes called a "demineralizer.") Elimination of radioactive coolant gases (which are produced continuously) is accomplished by venting them to special purification systems in a waste area.

WATER PROPERTY SENSORS

To maintain a water treatment system, sampling and analyses of chemical and physical properties of water must be applied at each step of the treatment processes. Water treatment is controlled primarily by instrument measurements and servo-systems (incorporating sensing elements and transducers).

Properties determined include:

- Dissolved oxygen.
- pH (acidity).
- Conductivity.
- Temperature.
- Flow rate.
- Radioactivity.
- Specific impurity (e.g., halides).
- Concentration.

CONDUCTIVITY MEASUREMENTS

A conductivity meter measures electrical current flow through a solution. And conductivity relates to the quantity of impurity ions. This sensor can be a simple glass jar containing two parallel plate electrodes (connected to a power source) in series with an ammeter. Any chemical compound that can be dissolved in water by ionization can be detected by the sensor.

DISSOLVED OXYGEN MEASUREMENTS

The most common dissolved oxygen meter sensors are solid state. Similar sensors are used to measure halide ions (chloride and fluoride).

HYDROGEN ION CONCENTRATION (pH) MEASUREMENT

Measurement of pH (degree of acidity or basicity) is made with a transducer; its electrical outputs are proportional to changes in negative logarithms of the hydrogen ion concentrations in water [$pH = -\log (H^+)$]. Pure water, at 77°F (25°C), contains both hydrogen and hydroxyl ions in equal concentrations of 10^{-7}moles/liter:

$$H_2O \rightleftharpoons H^+ + OH^-.$$

Equation 13-1-1
(Equation = Eq.)

Pure water has a pH of 7:

$$pH = -\log(10^{-7}) = 7.$$

Eq. 13-1-2

Scientists have found that the product of the hydrogen ion concentration and hydroxyl ion concentration at any pH is a constant (K_W):

$$\text{At } 77°F: \quad K_W = (H^+)(OH^-) = 10^{-14}.$$

Eq.13-1-3

At 500°F, approximately the operating temperature of BWR primary coolant, the constant K_w is equal to 10^{-11}:

$$K_w = (H^+)(OH^-) = 10^{-11}. \qquad \text{Eq. 13-1-4}$$

Hydrogen ion concentration in this solution is, therefore, equal to $10^{-5.5}$ moles/liter. Because pH is equal to the negative log of the hydrogen ion concentration at the operating temperature, Equation 13-1-5 shows that, at 500°F (in a BWR), with no chemical additives, the pH should be approximately 5.5:

$$pH = -\log (10^{-5.5}) = 5.5 \qquad \text{Eq. 13-1-5}$$

In a typical water-properties sensing system (Figure 13-1-4), the sensing element could be a pH electrode, a conductivity cell, or a halide electrode that produces an electrical signal, which is transmitted to a recorder or controller.

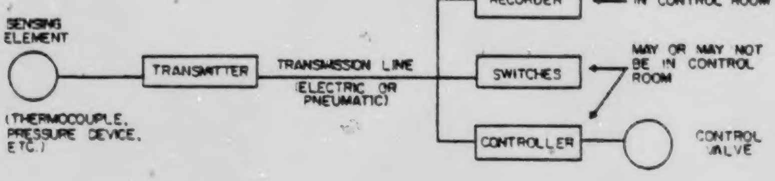

Figure 13-1-4. Water-properties sensing system.

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CHEMICAL ANALYSES

Other types of chemical analyses are required to monitor functions of a water treatment system. Some radiochemical and chemical analyses are performed daily on reactor coolant samples; for example:

Gross-beta and gross-gamma radiation (used as a measure of corrosion levels).

Chloride, fluoride and oxygen analyses (used as an index of corrosion potential).

Make-up water is tested before charging, or pumping, into reactor cooling system. Conventional wet-chemical methods are used for these types of analyses. Equipment might include burettes for titration, analytical balances for gravimetric analyses and spectrophotometers for colorimetric analyses.

Chemical data, used to define corrosion rates and other operational parameters, is also subject to regulatory requirements of the Nuclear Regulatory Commission (NRC). The NRC has final authority on some types, frequencies and, occasionally, locations of radioactive and other chemical sampling procedures; for example, NRC requires sampling of concentrations of radio-nuclides in effluents delivered to the environment.

EXERCISES

1. Name two impurities (in water) removed by chlorine.

2. If one liter of water dissolves 10 milligrams of soluble gas, determine the following:

   Solubility of gas (in ppm).
   Solubility of gas (in ppb).

3. If an ion exchanger is used to demineralize a natural water supply, why is well water more completely purified than river water?

4. If a water supply contains impurities (listed below), indicate whether or not the water treatment system shown in Figure 13-1-2 can remove each impurity:

Treatment System Figure 13-1-2	Dissolved Gases	Carbonate Hardness	Suspended Solids
Demineralization			
De-aeration			
Evaporation			
Lime-Soda			
Clarification			

MATERIALS

None.

PROCEDURES

None.

DATA TABLE

None

REFERENCE MATERIALS

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TEST

1. Explain individual effect (on a power plant cooling system) of each of the following impurities:

Chloride.

Fluoride.

Hydroxide.

Carbonate.

Bicarbonate ions.

Oxygen.

Carbon dioxide.

Color.

Living organisms.

2. List typical values for the following (include units):
Total solids.

Dissolved oxygen.

pH.

Conductivity.

3. Briefly explain each of the following processes:
Clarification.

Softening.

Chloration.

Filtration.

De-aeration.

Ion exchange.

Demineralization.

4. Briefly explain sensor operation for each of the following properties:

Conductivity.

Dissolved oxygen.

Hydrogen ion concentration (pH).

5. Define:

ppb.

Hard water.

Surface water.

Make-up water.

Anion.

Turbidity.

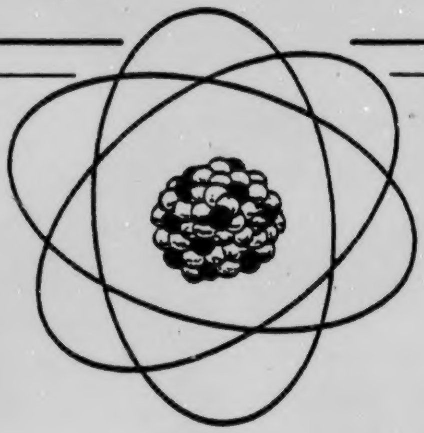
Ground water.

Dissolved solids.

Suspended solids.

Total solids.

Cation.



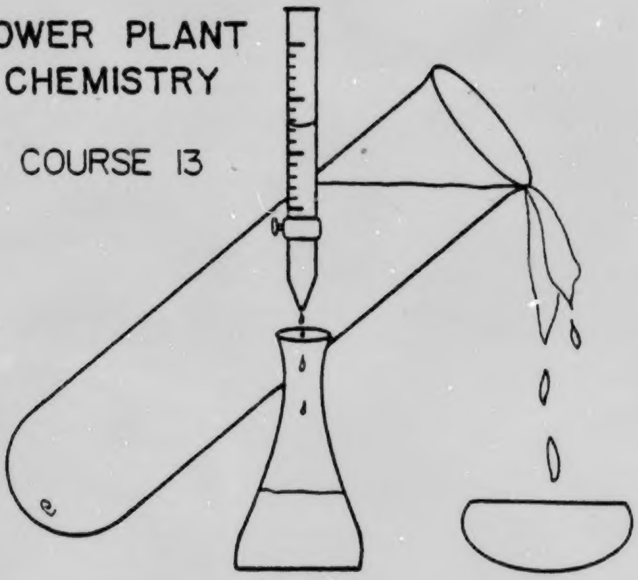
NUCLEAR TECHNOLOGY

MODULE 13-2 RAW-WATER TREATMENT. -

ROBERT B. NEEL

POWER PLANT CHEMISTRY

COURSE 13



TERC-SW

TECHNICAL EDUCATION RESEARCH CENTER — SOUTHWEST
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COURSE MODULES

COURSE 13 POWER PLANT CHEMISTRY

MODULE 13-1	Water Quality Control
MODULE 13-2	Raw-Water Treatment
MODULE 13-3	Sources of Impurities in Reactor Water Systems
MODULE 13-4	Water Treatment - Polishing by Ion Exchange, Evaporation and Demineralization
MODULE 13-5	Water Properties Sensing
MODULE 13-6	Water Analysis for Nuclear Power Plants
MODULE 13-7	Radioactive Waste handling - Liquid and Gaseous

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INTRODUCTION

Generally, raw water, as found in nature, is unacceptable as industrial water or as reactor cooling water. To produce industrial-use water, raw water must be treated to remove undesirable impurities by applying appropriate operations, techniques and processes normally associated with sanitary engineering.

The most common water treatment methods, discussed in this module, include clarification, filtration, chlorination, de-aeration and lime-soda softening. Because each source of raw water usually contains unqiue impurities, each treatment must be unique; also, not all techniques are always required in every instance. This module presents applications of the five most common methods of treating water presumed to contain turbidity, color, suspended and dissolved solids, gases, odors and algae. All of these contaminants are cause for concern to the operators of nuclear power plants.

MODULE PREREQUISITES

The student should have completed Module 1 (in this Course) and its prerequisites.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Describe briefly the theories of:
   - Filtration.
   - Coagulation.
   - Chlorination.
2. Define flocculation and describe briefly how it supplements coagulation.
3. List two operational problems in a clarification system.
4. Discuss briefly the two methods of chlorination of water:
   - Direct feed.
   - Solution feed.
5. List four operational problems in a chlorination system.
6. Sketch a fast-filter system and an ultrarapid pressure-filter system and briefly compare and contrast them.
7. List four operational problems in a filtration system.
8. List five major substances causing hardness in water.
9. Describe briefly the theory of water softening (use appropriate chemical equations).
10. Briefly describe water-softening processes.
11. Describe briefly the purpose of de-aeration and how it is accomplished.
12. Given appropriate materials and equipment, coagulate raw (dirty) water with alum.
13. Given appropriate materials and equipment, soften a quantity of hard water with soda lime.

OVERVIEW: RAW-WATER CONVERSION SEQUENCE

A typical sequence (Figure 13-2-1) of treatments for converting raw water into industrial water may begin with clarification (clearing), followed by filtration, chlorination, softening and de-aeration.

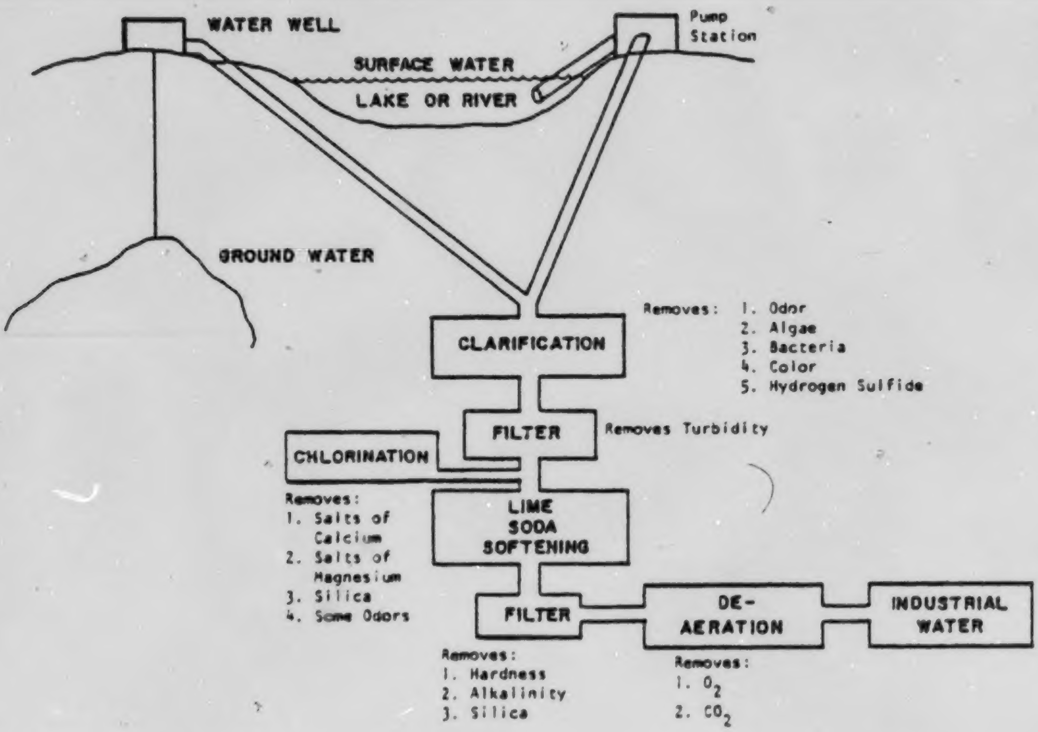

WATER WELL
Pump Station
SURFACE WATER
LAKE OR RIVER
GROUND WATER
CLARIFICATION
Removes: 1. Odor 2. Algae 3. Bacteria 4. Color 5. Hydrogen Sulfide
FILTER
Removes Turbidity
CHLORINATION
Removes: 1. Salts of Calcium 2. Salts of Magnesium 3. Silica 4. Some Odors
LIME SODA SOFTENING
FILTER
Removes: 1. Hardness 2. Alkalinity 3. Silica
DE-AERATION
Removes: 1. O2 2. CO2
INDUSTRIAL WATER

Figure 13-2-1. Typical steps in converting raw water into industrial water.

RAW-WATER CLARIFICATION

Foreign matter in water may be broadly classified according to its origin:

Inorganic mineral matter.
Organic matter.

Substances producing turbidity (cloudiness) are frequently inorganic minerals (mud or clay, for example), while substances producing color, taste and odor are mainly organic compounds (for example, decayed leaves or human sewage).

Particles producing turbidity can be subdivided further into two main groups:

Coarse.
Colloidal particles.

Coarse particles (such as sand and silt), with diameters greater than 10 microns (4/10,000 in), settle out of turbid water within a few hours. But particles with diameters less than 1 micron may remain suspended for weeks (or, sometimes, years) before settling out. These smaller particles are called "colloidal."

COAGULATION

Colloidal particles normally settle slowly, if at all, because of their minute size. Conceivably, they could coalesce (stick together) to form larger particles, which would settle more rapidly. Generally, however, they do not. Repulsion occurs between charged atoms (or molecules) that surround the charged colloidal particles in a water solution (Figure 13-2-2).

Addition of a coagulant, such as alum or ferric sul-

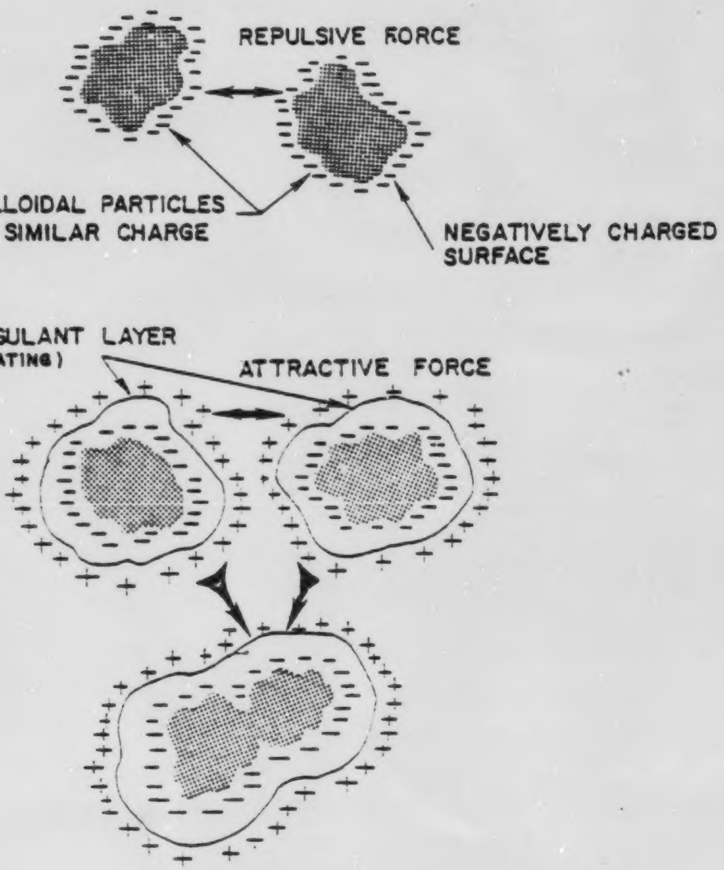

REPULSIVE FORCE
COLLOIDAL PARTICLES OF SIMILAR CHARGE
NEGATIVELY CHARGED SURFACE
COAGULANT LAYER (COATING)
ATTRACTIVE FORCE

Figure 13-2-2. Mechanisms of coagulation.

fate, to this colloidal suspension produces another colloid (of opposite charge). This colloid coats the original particles, partially neutralizing the charged layers surrounding each original particle, and reducing the force of repulsion. Particles then may adhere more easily to one another when they collide in solution. Thus, two particles can form a larger particle, and two of these larger particles can, in turn, form a still larger particle, until the range of interaction of electrical forces is exceeded.

The objective of this clarification process is to destabilize (neutralize) the colloids and to increase their average particle size and thereby obtain rapid settling (in seconds or minutes).

FLOCCULATION

Flocculation (floc) causes these small "clumps" of coagulated particles to form three-dimensional chemical structures by "bridging." Such chemical bridging can result in particles up to 2000 microns (0.08 in), which are gigantic in comparison with the original individual colloidal particles of less than 1-micron diameters.

Frequently, to produce "tougher" flocs that remain chemically bonded during rough handling (such as transfer from one container to another or during filtration), flocculation aids are used. The two most common are polyelectrolytes (called "polymers") and activated silica. These synthetic chemical compounds contain repeating units of small molecular weight, chemically combined to form a long-chain molecule of colloid size. Each repeating unit carries one or more electrical charges, and provides a means of increasing floc size when water quality changes from normal (or for cold-weather conditions).

Charged sites on a polymer reach out like "arms" to oppositely charged sites on individual colloidal particles to form a long chain. These chains combine three-dimensionally to form giant floc.

(Note: An optimum range of polymer concentration exists: too little leads to a "weak" floc; too much results in floc dispersion. Like most water treatment methods, appropriate concentration usually is determined empirically for the specific water under treatment.)

TYPICAL COAGULATION PROCESSES

The single most important parameter in clarification (coagulation) is pH (i.e., the negative natural logarithm of a hydrogen ion concentration, written -log H+). For removal of turbidity, best results normally are obtained in a pH range between 6.0 and 7.8. For removal of color, the preferred range is from 4.0 to 6.0. If the solution is too acidic (low pH), gelatinous precipitate, which comprises the main ingredient of the coagulant, cannot form.

Aluminum sulfate and iron sulfate are typical coagulants. They normally are added to a coagulation basin as liquids, along with a lime solution to supply basicity to adjust the pH appropriately for the precipitation process to occur, as follows:

$$Al_2(SO_4)3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4.$$

Equation 13-2-1
(Equation = Eq.)

In an alum coagulation, the precipitated aluminum hydroxide reacts to form a positive colloid:

$$8Al(OH)_3 \rightarrow [Al_8(OH)_{20}]^{4+} + 4OH^-.$$

Eq. 13-2-2

Solution basicity (pH) is important because of the sulfuric acid formed as a result of Equation 13-2-1 and because of the hydroxyl ion formed in Equation 13-2-2.

Iron salts are also commonly used as coagulants with lime:

$$Fe(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3\downarrow + 3CaSO_4.$$

Eq. 13-2-3

Formation of an iron hydroxide precipitate, similar to the formation of aluminum hydroxide, precipitates over a wider range of pH. When either forms a floc, it settles rapidly, carrying suspended solids (including colloids) and color down with them to produce a sludge.

SLUDGE SEDIMENT EQUIPMENT

To obtain clarified (clear) water, floc must be allowed to settle (undergo sedimentation) before the clear fluid above the sludge is drawn off. In recent years, basins that combine coagulation, flocculation, settling and sludge removal all in a single unit have become popular. These multiple-use units are frequently referred to as "clarifiers."

In a typical continuous-process clarifier (Figure 13-2-3), water enters from an inlet (right side) into a flash mixer (1) where it is mixed rapidly with coagulants by a rotating stirrer. Water, coagulant and finely dispersed precipitates are then given gentle mixing as they flow through rotating paddles in the flocculator (2). The settling basin (3) receives this mixture from the flocculating

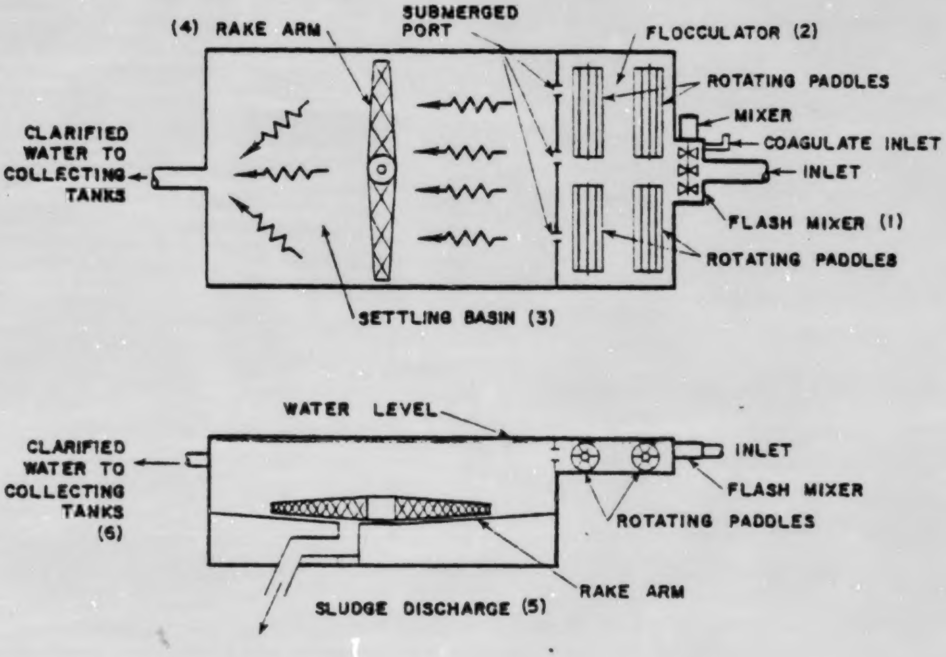


Figure 13-2-3. Continuous-process type clarifier.

chamber through submerged ports. The basin is equipped with a rotating vertical shaft with radial arms and rake blades that just clear the tank bottom (4). Sludge, which has settled from the water, is raked inward to a central discharge hopper and removed continuously (5). Clarified water then flows into a collecting tank (6).

In a smaller capacity clarifier, of the sludge-blanket type (Figure 13-2-4), raw water enters the main mixing tank (3) through the inlet (1). In the lower part of the central shaft, water is mixed with treatment chemicals and recirculated sludge from the bottom of the unit. This mixture of water and chemicals is forced through a central uptake pipe by a variable-speed agitator (2), where coagulation reac-

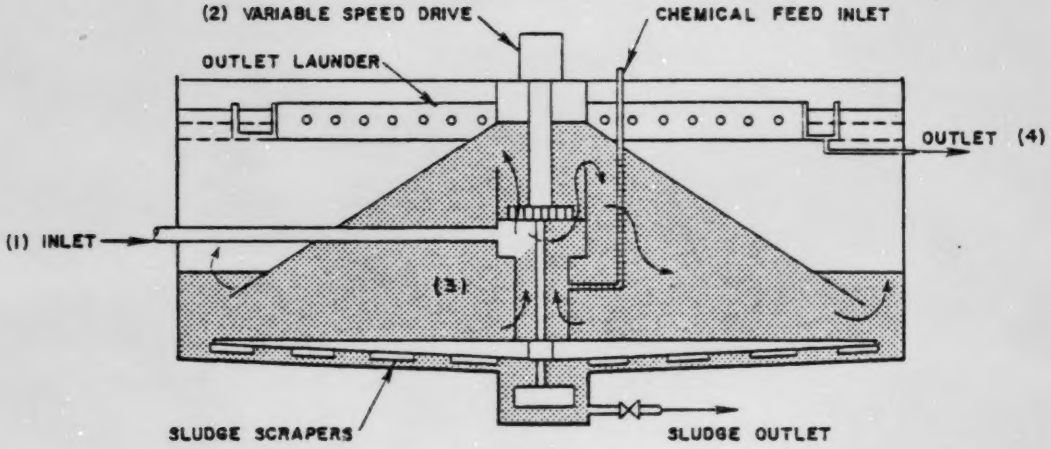


Figure 13-2-4. Sludge-blanket type clarifier.

tions are brought to completion. Some water and suspended precipitates enter the lower end of the uptake for recirculation and make contact with incoming chemicals and raw water. New floc formation is encouraged by contact with previously formed precipitates. Clarified water rises to the outlet (4) and heavier particles settle to the bottom to be removed as sludge.

COMMON CLARIFIER OPERATIONAL PROBLEMS

The most common clarifier operational problem is improper control of solution pH, which results in incomplete, inefficient coagulation.

A second problem results from insufficient amounts of coagulant being applied, leaving a "weak" floc. The filtrate retains dissolved ions and the floc breaks into fragments that do not filter well in rapid-sand or demineralizer type filters. Occasionally, an operator who observes that a little added polymer works well will add an excessive amount, hoping the excess will work better. But it merely disperses the floc, particularly in large mixing basins in which time required to mix the coagulant (polymer) into the main solution mass is underestimated by the operator. For example, a moderate-sized basin, containing 18,000 cubic feet of solution into which a centrifugal pump delivers 50 gallons per minute, requires about 50 minutes just to turn the solution over once; good mixing may require several hours; therefore, the smaller the tank and the greater the flow rate, the less significant this problem becomes.

RAW-WATER CHLORINATION

Chlorine frequently is introduced into a mixing basin during coagulation, as a disinfectant. (Raw water may contain bacteria, algae and viruses, which must be removed if the water is to be used for drinking or for biological applications.) Furthermore, algae, under proper conditions of pH and with proper nutrients, can greatly multiply their biomass in such a way as to plug pipes or the pores of filters, disrupting flow and filtration processes. The problem of algae growh is also rather common when using sea water as the cooling medium for turbine condensers in power plants.

Chlorine injection equipment is designed to control and meter chlorine (in the gaseous state) and to apply it either as a gas or as an aqueous chlorine solution. There are two principal methods of application of chlorine gas:

"Direct-feed," which involves metering dry chlorine gas and conducting it to the water being chlorinated.

"Solution-feed," which involves metering dry chlorine gas into a proper amount of water to prepare a liquid concentration and pumping it into a coagulation basin (or other receiver).

The solution-feed method, using a "vacuum" feeder (Figure 13-2-5) is more popular. Its chlorinator contains some type of gas flow-controller, such as a metering orifice. (A typical feeder might supply 500 pounds of chlorine in 24 hours.) The gas passes to a water-operated, aspirating-type ejector in which gas is mixed with a small quantity of water prior to injection into the solution to be chlorinated.

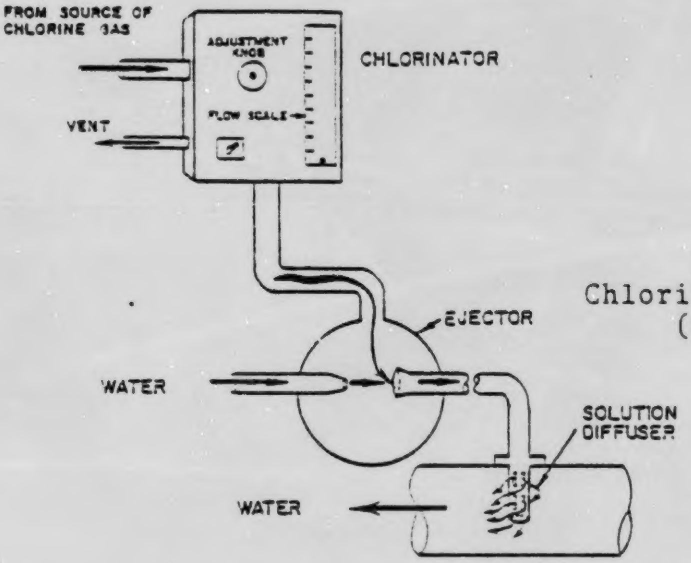


Figure 13-2-5.
Chlorine solution feeder (vacuum type).

The solution diffuser, which mixes the concentrated chlorine solution with the solution to be treated, may be nearby or hundreds of feet away from the ejector.

A vent protects operating personnel, during shutdown, should chlorine discharge to the atmosphere. Concentrations of chlorine normally used to remove algae and other contaminants are 3 to 5 p/m, if the contact time of chlorine concentrate with the solution to be treated is between 15 and 30 minutes. The chemical reaction of chlorine gas with an odor-producing sulfide gas is shown in Equation 13-2-4:

$$H_2S + 4C\ell_2 + 4H_2O \rightarrow H_2SO_4 + 8HC\ell. \qquad \text{Eq. 13-2-4}$$

Other chemical reactions remove slime (caused by bacteria, algae and other biological organisms).

OPERATIONAL PROBLEMS WITH CHLORINATORS

Common operational problems encountered with a chlorinator include:

- Floc or other coagulated mass may plug chlorine diffuser, reducing chlorination rate and modifying chlorine concentration in the solution to be treated.
- Normally, chlorine is stored under pressure as a saturated liquid in equilibrium with its vapor. Heat is sometimes required to stimulate chlorine gas flow eductor.
- When the heater coil burns out, gas flow stops.
- Moist chlorine gas corrodes metal parts.
- The chlorine relief vent may become clogged, which could present a hazard to personnel and cause equipment damage if the toxic gas leaks into the system.

FILTRATION OF CLARIFIED WATER

Smaller particles of floc, not removed in the clarifiers, must be filtered out. Most widely used is the mechanical rapid-sand filter (Figure 13-2-6). Dissolved solids, colored water, floc particles, dissolved chlorine and odorous substances enter this filter at the top and flow vertically downward through several layers of sand and a layer of gravel. The sand is in a bed about 3 feet (1 meter) deep; the gravel layer at the bottom is about 6 to 12 inches (15 to 30 cm) deep. Several different sizes of gravel are used, ranging from coarse stones at the bottom to particles about 0.1 inch (0.25 cm) in diameter at the top. This diminishing size of filtering media first spreads the floc uniformly throughout the sand bed area and then supports the sand so

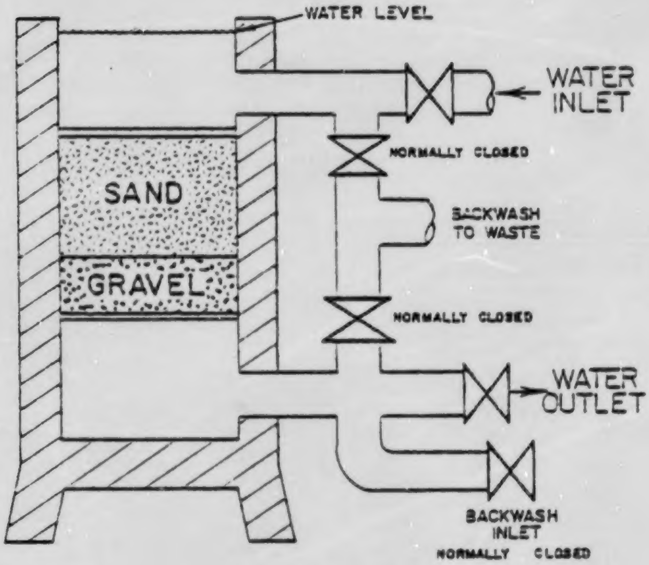


Figure 13-2-6. Rapid-sand filter.

that it does not pass out through the bottom of the bed during filtration.

Filtration rates are nominally about 2 gal/min/ft^2 of bed surface (49 liters/min/m^2).

Media other than sand may be used, such as charcoal, which reduces chlorine and odor levels to an acceptable minimum. Raw coal is used sometimes.

For "ultrarapid filtration" (8 to 15 gal/min/ft^2), the filter media can be graded from coarse to fine (opposite to the above) in the direction of the water flow. The depth of the deep bed is doubled, to about 7 feet (2 meters), and the water to be filtered is introduced under pressure (Figure 13-2-7). In this filter, as well as the previous type, provision must be made for "backwash."

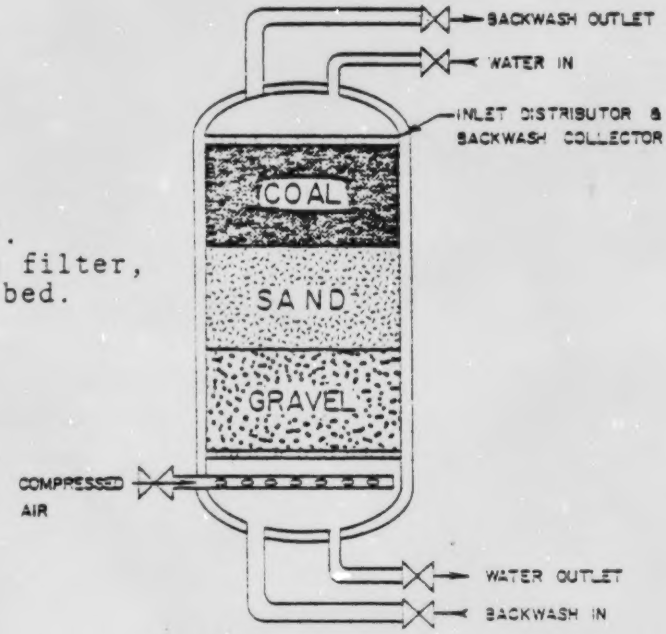


Figure 13-2-7.
Ultrarapid pressure filter,
dual multimedia bed.

Backwash is a stream of clear water introduced in direction opposite of flow of water to be filtered. This stream washes out solid, fine particles trapped in the top 3 inches (7.6 cm) of the filter during filtration. (Compressed air assists in dislodging particles.)

COMMON FILTER OPERATIONAL PROBLEMS

The most common operational problems associated with rapid-sand filtration include:

With age, the sand bed develops cracks along side walls of container, resulting in bypass of filter.

Large, flocculated particles, which remain within inches of the bed top, cause rapid buildup of pressure across the filter, leading to shortened lifespan.

Backwash flow rate, if set too high by operator, produces jets of water in sand bed.

Bed uniformity, if disturbed, leads ultimately to channels in bed, and bypass of filter.

Occasionally, backwash does not remove filtered matter, resulting in a clogged bed.

LIME-SODA SOFTENING

Lime-soda softening is commonly applied to remove some types of odor, silicas (sodium silicates), dissolved salts of calcium and magnesium, bicarbonates and sulfate salts, all of which produce water hardness and boiler scale. Calcium and magnesium bicarbonates are commonly referred to as "alkalinity" or "bicarbonate hardness." The sulfate salts of calcium and magnesium are commonly referred to as "noncarbonate hardness."

THEORY OF LIME-SODA SOFTENING

Lime, $Ca(OH)_2$, is added to an effluent to remove carbonate hardness, as shown in Equations 13-2-4 through 13-2-6:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O. \qquad \text{Eq. 13-2-4}$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + 2H_2O + MgCo_3. \quad \text{Eq. 13-2-5}$$

$$MgCO_3 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + Mg(OH)_2. \qquad \text{Eq. 13-2-6}$$

In Equations 13-2-4 and 13-2-5, lime removes the dissolved calcium and magnesium ions as insoluble calcium carbonate. The slightly soluble magnesium carbonate is removed with additional lime, as shown in Equation 13-2-6.

Both soda, Na_2CO_3, and lime are required to remove noncarbonate hardness. Equations 13-2-7 and 13-2-8 show how lime and soda remove the calcium and magnesium ions that are dissolved in raw water as sulfates:

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaSO_4. \qquad \text{Eq. 13-2-7}$$

$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$. Eq. 13-2-8

Carbon dioxide, which has dissolved from the atmosphere or rock strata, is also removed by lime:

$CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$. Eq. 13-2-9

Silica, dissolved sodium silicate, is partially removed as insoluble magnesium silicate:

$Mg(OH)_2 + Na_2SiO_3 \rightarrow MgSiO_3\downarrow + 2NaOH$. Eq. 13-2-10

Precipitation processes in Equations 13-2-4 and 13-2-5 produce water with no residual dissolved solids. But the processes in Equations 13-2-7 and 13-2-8 leave the total dissolved solids content changed only in composition. The sodium and calcium sulfates have a higher solubility than the calcium sulfates at the reactor operating temperatures and are, therefore, less likely to form deposits.

After the softening processes, the liquid effluent still contains dissolved gases, oxygen, some carbon dioxide, and so on, that also need to be removed.

LIME-SODA SOFTENING EQUIPMENT

Lime-soda softening equipment is similar in construction to clarification equipment because both processes incorporate precipitation to form sludges. In a sludge contactor softener (Figure 13-2-8), lime and soda are intro-

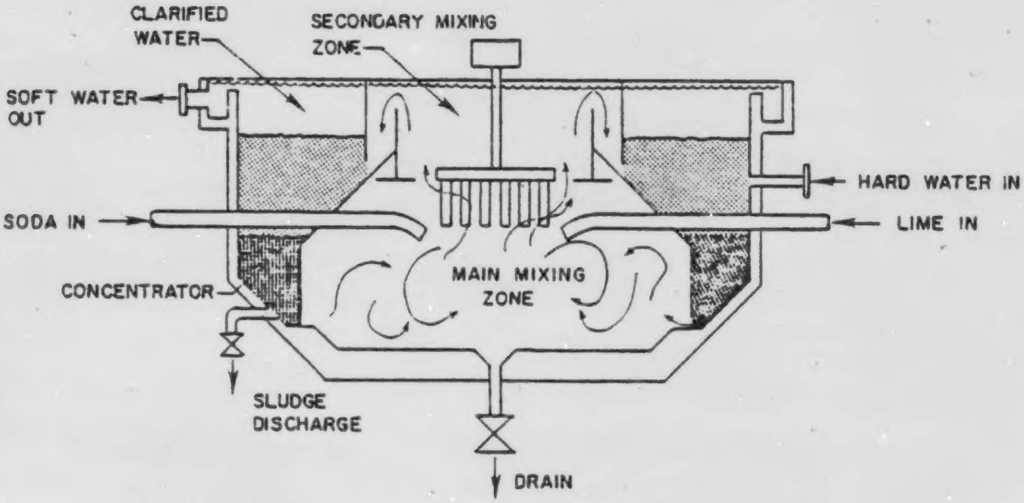


Figure 13-2-8. Sludge contactor softener.

duced as liquids at the top of the primary mixing and reaction zone. The precipitations described in Equations 13-2-4 through 13-2-10 take place in the primary mixing zone while the motor stirs the solution.

The swirling action of the impeller mixes the "aged" sludge with the "new" sludge to promote particle size growth. This action also causes the sludge mixture to pass into the secondary reaction zone where additional precipitation and more particle size growth can occur. Sludge contact time is normally 60 to 90 minutes, after which the heavy sludge settles into a concentrator, and the clear effluent passes on to the next step in the purification process (polishing by ion exchangers or demineralizers).

This softening process can be operated under either ambient or heated (hot) conditions. The same chemicals are used in both systems, but the hot process uses steam to heat the reaction mass to 212°F (100°C). This elevated temperature accelerates precipitation as well as growth phases so that only a 15-minute sludge contact time is normally required. Also, in the hot softening process, residual concentrations of dissolved ions are approximately half as large as in the cold process.

The total solids content of water that has been reduced by clarification, filtration and softening can be reduced still further by removing dissolved gases.

SOFTENED WATER DE-AERATION

De-aeration reduces concentrations of dissolved gases and removes some volatile organic matter. The water to be de-aerated is delivered as a fine spray onto a metal surface heated by process steam (Figure 13-2-9).

Gases dissolved in water bubble off and are vented to the atmosphere, while de-aerated water settles to the bottom to be pumped to the next purification step (demineralization).

When a significant amount of organic matter is not removed by the de-aeration process, granular carbon beds may follow the de-aeration system. The carbon also removes any last traces of chlorine, which could react with the demineralizers in the reactor cooling water make-up system.

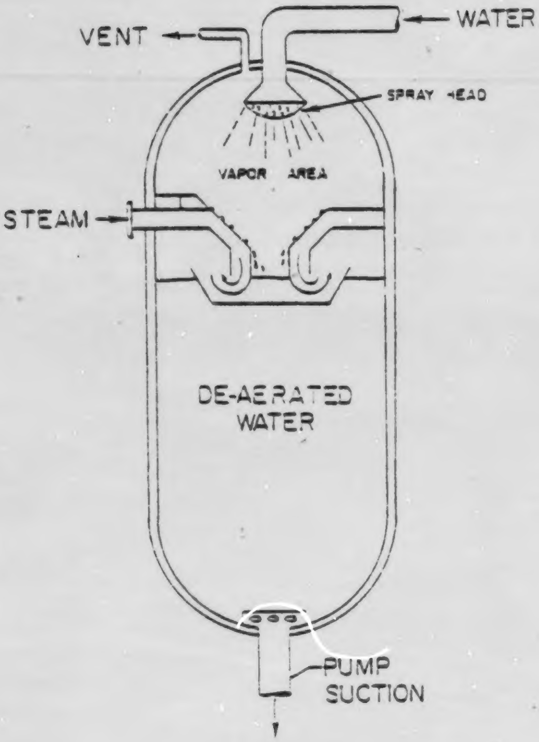


Figure 13-2-9.
Steam de-aerator.

EXERCISES

1. An operator notices that turbidity (of water leaving a settling basin of a clarifier) is increasing slowly. What operational problem should be suspected and checked first? Why?
2. If a chlorinator delivers 1.0 pound/hour of gas to a flowing stream of water to be disinfected, what is minimum flow rate (cfm) allowed if chlorine concentration cannot exceed 5 p/m? (Hint: Density of water is 62

pounds/cubic foot.)

3. How many pounds of lime are required to form 100 pounds of the gelatinous coagulant aluminum hydroxide in a clarifier containing 50,000 cubic feet of solution? (Assume that 100% excess lime is to be used.)
4. In a rapid-sand filter, what surface area is required to filter 60,000 liters/day of clarified water? What is filter capacity? How many gal/min of water are filtered daily?
5. How many grams/hour of soda must be fed to a lime-soda softener to remove 150 p/m from water flowing from the softener at 1000 gal/min?
6. Sketch a flow diagram for a typical raw-water or industrial-water conversion process. Identify each item and its purpose (what does it remove?).

MATERIALS

5 beakers (or jars) - 750 ml each.
5 magnetic stirring apparatus (if available).
1 set of pH papers.
1 100-ml pipette (graduated).
Stock solutions of:
    Alum - 1 gram to 1 liter water.
    Lime - 1 gram hydrated lime to 1 liter distilled water.

PROCEDURES

Part I

1. Fill a container (of any kind) with 1 gallon (3.8 liters) of tap water. Add a generous handful of dirt. Shake well.
2. Measure 500-ml portions of this dirty (turbid) water into each of the 5 beakers. Check and record pH on Data Table 13-2-1.

Part II

3. As a preliminary test, add about 30 ml of alum stock solution to one of the beakers of turbid water. Stir well.
4. Check solution with pH papers (pH should be between 6 and 8).
5. If pH is too low, add 1 ml of lime stock solution, while stirring vigorously.
6. Remeasure pH. Add more lime stock solution if necessary to obtain desired pH range, as mentioned in text.
7. If no precipitate forms in 5 minutes, repeat steps 3 through 6, add 15 ml more of alum stock solution. Note results.

Part III

8. Arrange the other four beakers in a line. Label them: raw water No. 1, No. 2, No. 3 and No. 4.
9. Quickly add graded amounts of alum to each beaker, as shown in Part II above.
10. Add lime stock solution to obtain a pH between 6 and 8 in each beaker.
11. Add magnetic stirring bars, if available, and turn on the stirrers. Otherwise, stir each solution manually

for about 20 minutes (alternating stirring between all jars).

12. At end of flocculation period, observe color of clear fluid above precipitate; record on Data Table 13-2-2 the color as 1) none, 2) light, 3) moderate or 4) dark.
13. Measure height (in centimeters) of clear fluid above floc. Record on Data Table 13-2-2, column 5.
14. Select best dose of alum coagulant from data in Data Table 13-2-2 (clearest fluid and greatest fluid height).

DATA TABLE

DATA TABLE 13-2-1
PRELIMINARY DATA

		Test 1	Test 2	
1	Milliliters of turbid water			ml
2	Milliliters of alum stock solution added			ml
3	pH of solution in step 2			pH
4	Milliliters of lime stock solution added to give pH 6 to 8 for solution in step 2			ml

DATA TABLE 13-2-2
TEST DATA

No. of Beaker	Alum* Dose in p/m	Lime* Dose in p/m	Result of Flocculation	
			Color	Height
-	0	0		
1	10			
2	20			
3	40			
4	60			

* 1 milliliter of stock solution added to 500 milliliters of water gives a dose of 1 mg/0.5 liters, or 2 p/m.

REFERENCE MATERIALS

American Water Works Association, Inc. Water Quality and Treatment: A Handbook of Public Water Supplies. 3rd ed. New York: McGraw-Hill Book Co., Inc., 1971.

Cox, C.R. "Operation and Control of Water Treatment Processes." World Health Organization Monograph Series 49 (1964).

TEST

1. Describe briefly the theory of each of the following:

   Filtration.

   Coagulation.

   Chlorination.

2. Define flocculation and describe how it supplements coagulation:

3. List two operational problems in a clarification system:

4. Discuss briefly direct-feed and solution-feed methods of water chlorination:

5. List four operational problems in a chlorination system:

6. Sketch a fast-filter system and an ultrarapid pressure-filter system; compare and contrast them in one paragraph:

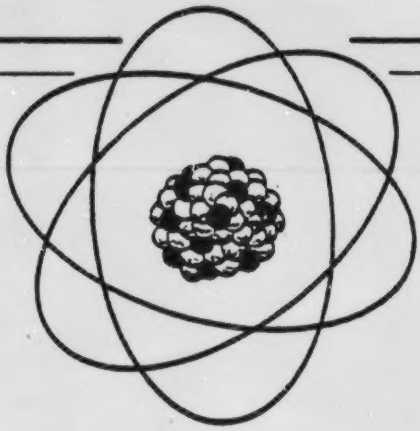
7. List four operational problems in a filtration system:

8. List five major substances causing hardness in water:

9. Briefly describe theory of water softening by use of appropriate chemical equations:

10. Describe in one or two sentences lime-soda softening:

11. Briefly describe the purpose of de-aeration and how it is accomplished:



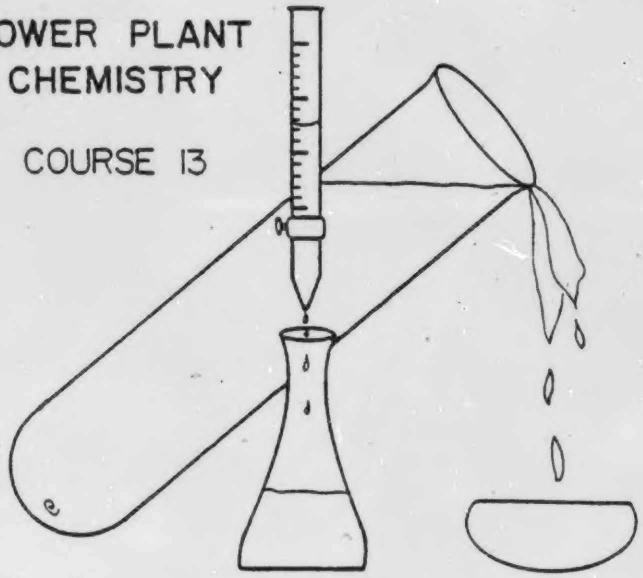
NUCLEAR TECHNOLOGY

MODULE 13-3 SOURCES OF IMPURITIES IN REACTOR WATER SYSTEMS. -

ROBERT B. NEEL

POWER PLANT CHEMISTRY

COURSE 13



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TECHNICAL EDUCATION RESEARCH CENTER — SOUTHWEST
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COURSE MODULES

COURSE 13 POWER PLANT CHEMISTRY

MODULE 13-1	Water Quality Control
MODULE 13-2	Raw-Water Treatment
⇨ MODULE 13-3	Sources of Impurities in Reactor Water Systems
MODULE 13-4	Water Treatment - Polishing by Ion Exchange, Evaporation and Demineralization
MODULE 13-5	Water Properties Sensing
MODULE 13-6	Water Analysis for Nuclear Power Plants
MODULE 13-7	Radioactive Waste Handling - Liquid and Gaseous

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INTRODUCTION

To obtain maximum heat transfer and most efficient use of reactor fuel during power generation, suspended and dissolved solids in reactor coolant must be minimized. For example, if only one part per billion (ppb) of metal is dissolved continuously from the walls of a feedwater heater (in a BWR), more than 100 pounds of scale can be redeposited in the reactor core and piping in a year's time. These deposits (scales) can become radioactive, and they can be redeposited on coolant surfaces outside the core, creating a radiation exposure problem for maintenance personnel.

This module describes the major mechanisms for formation of dissolved and suspended corrosion products in a PWR or BWR. It also deals with the effects of impure reactor coolant.

MODULE PREREQUISITES

The student should have completed the following modules in this Course: 13-1, "Water Quality Control," and 13-2, "Raw-Water Treatment."

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Define or describe:
    - Boiler scale.
    - Steam carryover.
    - Corrosion.
    - Activation product.
2. List two common methods used to reduce boiler scale.
3. Describe carryover and why it may cause significant problems in a power plant steam generator.
4. List methods used to reduce steam carryover.
5. Briefly explain:
    - Erosion.
    - Uniform corrosion.
    - Galvanic corrosion.
    - Crevice corrosion.
    - Pitting.
    - Intergranular corrosion.
    - Stress-corrosion cracking.
    - Fretting.
    - Cavitation.
6. Describe corrosion mechanisms applicable to metals.
7. Describe methods used to reduce corrosion in reactor metals 1) at the design stage, 2) by selection of proper materials and 3) during operations.
8. List major sources of activation products in the reactor coolant.
9. List range of particle sizes and composition of typical crud.
10. Describe mechanisms proposed for release and transport of radioactive substances, within coolant.

11. Describe mechanisms for accumulation of fission products in reactor coolant feedwater.
12. Illustrate, by experiment, effects of various compositions of water on corrosion rate of reactor metals.

SCALE CONSEQUENCES

Formation of scale and sludge deposits on boiler heating surfaces is the most serious water problem encountered in steam generation.

It can cause mechanical fouling of flow channels through the reactor core, increasing pressure drop across the core, resulting in reduced operating power.

Boiler scale presents a resistance to heat removal from fuel pellets; therefore (more serious than fouling), overheating of the reactor fuel can develop, resulting in a greater probability of cladding failure.

Similar overheating may occur in the condenser, or steam generator, if their tubes are coated with a scale film. And the probability of their failure is increased greatly.

Failure, in any of the critical areas, is apt to require the reactor to be shut down for maintenance at great cost to the utility.

SCALE FORMATION CAUSES

Scale formation occurs when the solubility tolerance of chemicals dissolved in boiler water are exceeded at boiler temperatures. The chemicals precipitate out of the circulating coolant water and slowly form deposits on rough surfaces or joints within the metal piping. Eventually it bakes in place, forming hard scale. Precipitation occurs preferentially at local hot surfaces because the liquid surface film tends to become more concentrated than the main stream of boiler water. Solubility of scale-forming salts is exceeded first at these hot surfaces.

Salts of calcium and magnesium are the most common sources of scale-forming impurities in water. The solubility of these two impurities decreases with increasing temperature (Figure 13-3-1).

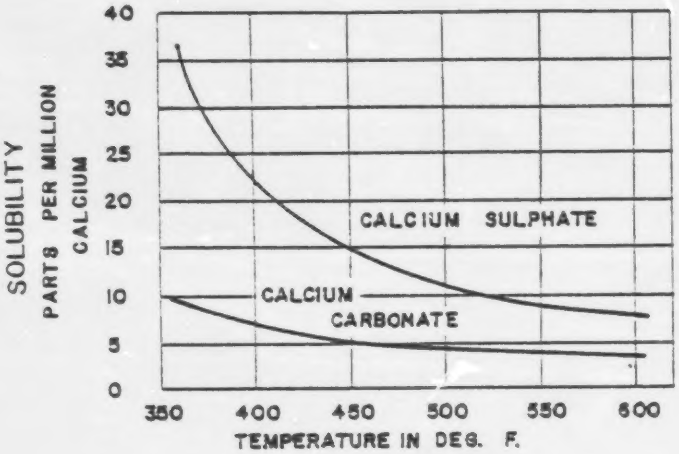


Figure 13-3-1.
Solubility of common scale-formers.

EXAMPLE

Given: Makeup water, containing 36 ppm of calcium sulfate at 360°F, is pumped into a boiler (operating temperature: 600°F), solubility decreases from 36 ppm to 8 ppm, a difference of 28 ppm; makeup (flow rate) of reactor water is 100 gpm.

Find: Quantity of solids (Qs) available for deposit in system.

Solution:

$$Qs = 100 \text{ gal/min} \times \frac{1 \text{ ft}^3}{7.5 \text{ gal}} \times \frac{62 \text{ lb}}{\text{ft}^3} \times 28 \text{ ppm}$$

$$\times 1440 \text{ min/day}$$

$$= 33 \text{ lb additional } CaSO_4\text{/day.}$$

BOILER SCALE REDUCTION METHODS

To minimize solids deposits on reactor primary (or secondary) surfaces, raw water used for filling the circulating cooling loops (makeup water) must be treated. In addition, continuous treatment of the recirculating coolant is necessary.

CARRYOVER

In addition to deposits, which can form on the piping and the heat transfer surfaces, another type of deposit is sometimes formed on the turbine blades by a phenomenon called steam carryover. In the pressure vessel of a BWR, or in the steam generator of a PWR, turbulent boiling occurs. This violent motion of liquid produces droplets by cavitation that are small enough to be carried by fast flowing steam (gas) into the turbine steam lines. These liquid droplets, if not removed, collide violently with the fast rotating turbine blades, causing *erosion* of the metals, much as sandblasting erodes stone.

Some droplets contain dissolved solids. Some droplets evaporate on the hot turbine blade surface, leaving a film or deposit (called solids carryover). Such a buildup of solids eventually will cause turbine imbalance which can lead to costly maintenance problems. Solids may also deposit on valve seats or other contact points, preventing them from operating properly.

Low-quality cooling water frequently contains considerable amounts of dissolved silica (H_3SiO_3). This silica is carried over either as a vapor or dissolved in droplets. In a PWR secondary system and in a BWR primary system, almost all the carryover of silica is by liquid droplets.

Carryover generally is eliminated by using moisture separators (demisters) placed above the boiling water. Steam must pass through them before leaving the pressure vessel (steam generator). As the gas twists and turns through the baffles within the demisters, it collides with solid surfaces, where it condenses and drips back into the boiler.

COMMON FORMS OF METAL CORROSION

The most common impurities in reactor water are the *corrosion* products of metals that make up the reactor structures and the fuel cladding. Reactor metals can corrode by either chemical or mechanical mechanisms.

CHEMICAL ATTACK ON REACTOR METALS

The most common forms of chemical corrosion in reactor water systems involve the following processes:

Uniform corrosion.
Galvanic corrosion.
Crevice corrosion.
Intergranular corrosion.
Pitting corrosion.
Stress-corrosion cracking.

Uniform Corrosion

Uniform corrosion occurs at a fixed rate on every part of a metal surface. Common examples of uniform corrosion by oxygen are the tarnishing of silver or the oxidation of a piece of iron to form red rust. Uniform corrosion can be demonstrated in the laboratory with a piece of steel in a container of dilute hydrochloric acid. The metal will dissolve uniformly over the entire surface of the steel (Figure 13-3-2).

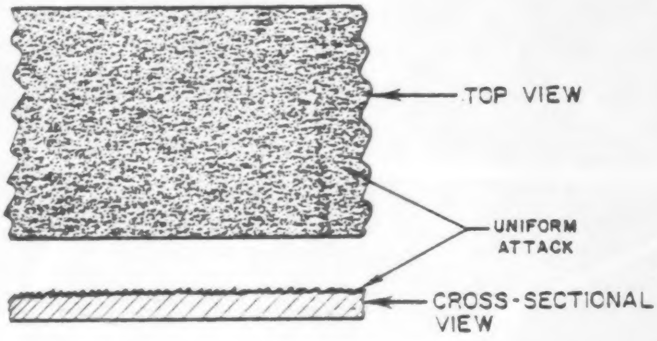


Figure 13-3-2.
Uniform corrosion.

Uniform corrosion rate is customarily measured in milligrams of metal loss per month based on one square decimeter of surface (i.e., $mg/dm^2/mo$). Another common unit of measure is mils per year (i.e., thousandths of an inch per year) - obviously a very slow rate of corrosion that, even with the large surface areas exposed in a reactor, normally does not cause structural weakening. Sometimes a corrosion allowance is added to metal-thickness design to offset structure weakening within a given period of time; however, the corrosion does introduce corrosion product impurities.

Galvanic Corrosion

Galvanic corrosion occurs when two dissimilar metals are immersed in a conducting solution and, thereby, electrically connected externally - an electro-chemical process, much like that in an auto battery. In another example (Figure 13-3-3), aluminum metal dissolves in electrolyte

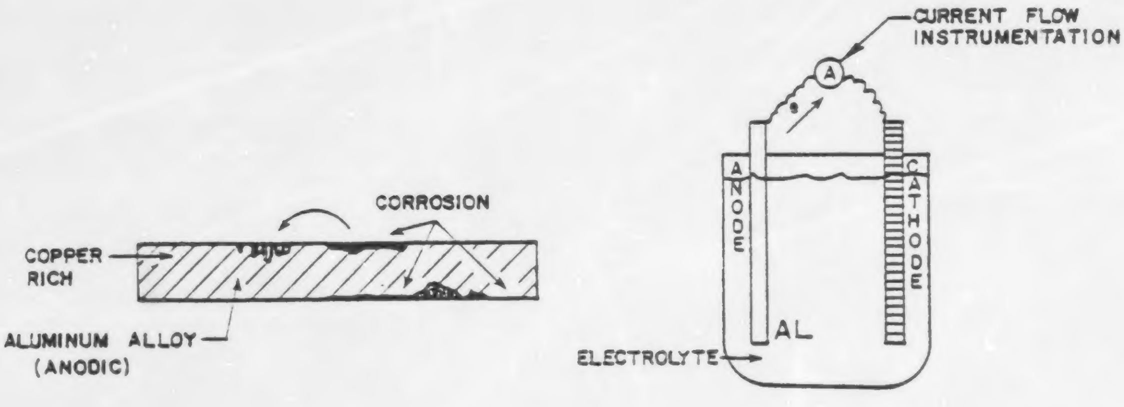


Figure 13-3-3. Galvanic corrosion.

(conduction solution) at an electrode (called an anode). Electrons travel through external wires to the copper electrode and then to the cathode, where hydrogen ions (always present in water) accept them and form hydrogen gas. The net effect of this process is to thin down the aluminum electrode.

It is possible to roughly predict which metal in an alloy will preferentially corrode by using a galvanic series (Table 13-3-1). A metal near the top of the list, when alloyed (or in contact) with a metal near the bottom, corrodes more rapidly than when alloyed or in contact with

TABLE 13-3-1

GALVANIC SERIES OF REACTOR METALS (IN SEA WATER)
Proceedings of the American Society for
Testing Materials, 40, 670 (1940).

ANODIC	Wrought Iron	
	Carbon Steel	
	316 Stainless Steel	active forms
	304 Stainless Steel	
	Tin	
	Lead	
	Inconel (active form)	
	Copper	
	Admiralty Brass	
	70-30 Copper-Nickel	
	Monel	
	Inconel	passive forms
	315 Stainless Steel	
	304 Stainless Steel	
CATHODIC	Platinum	

* Proc. Amer. Soc. for Testing Materials, 40, 670 (1940).

metal close by in the list. For example, a steam generator (PWR) has heat-exchange tubes constructed of Inconel; these tubes are supported by carbon steel tube-sheets. From the spread given in Table 13-3-1, some galvanic corrosion may be expected (carbon steel is widely separated from Inconel in the list). On the other hand, less corrosion is apt to occur if the Inconel tubes are supported by a stainless steel tube-sheet.

Galvanic corrosion is usually prevented or reduced by one of three methods. First, the designer (an architect-engineer) may choose metals close together in the galvanic series for surfaces that contact each other or share a conductive environment (e.g., water). Second, metals far apart in the series may be used if their points of contact are electrically insulated. Finally, the surface of one metal may be coated with a film that is unreactive to the other metal. Copper has such a film (copper oxide), which renders it unreactive (passive) in water solutions.

Generally, all of these methods are used somewhere in every reactor water system.

Crevice Corrosion

Crevice corrosion commonly occurs where metal parts join at seams (e.g., at weld points, or on ball bearing surfaces, causing them to seize). Crevice corrosion is less of a problem in a PWR - hydrogen gas dissolved in the coolant keeps oxygen levels to negligible concentrations. In a BWR, however, hydrogen can become depleted (for example, in a crack, or in an annular space between an infrequently used pump shaft and its sleeve). This lack can set up corrosion currents, which thin out the metal.

This type of corrosion, if not eliminated at the design stage, is usually controlled at the plant by three processes:

Physically closing existing crevices (with welds, solder, caulking or other means).

Keeping mating surfaces in motion.

Keeping pH high and oxygen content low.

Pitting

Pits, or holes, form in metal surfaces when its protective film (passive surface, on a metal) is disturbed (Figure 13-3-4).

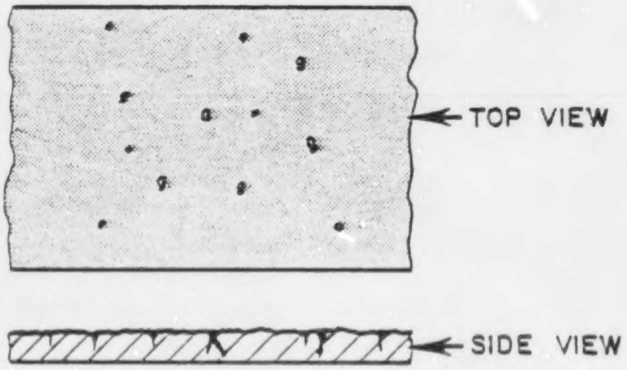


Figure 13-3-4. Typical pitting corrosion.

Why pitting begins is often difficult to determine. But, once begun, corrosion products accumulate in the holes and the pitting process accelerates.

For those systems other than the primary and secondary systems of the reactor, chromates are sometimes added to inhibit this corrosion process. The chromates coat the metal surface and make it passive toward the prime corrodant, oxygen.

Intergranular Corrosion

Intergranular corrosion takes place along the grain boundaries between metallic crystals (Figure 13-3-5).

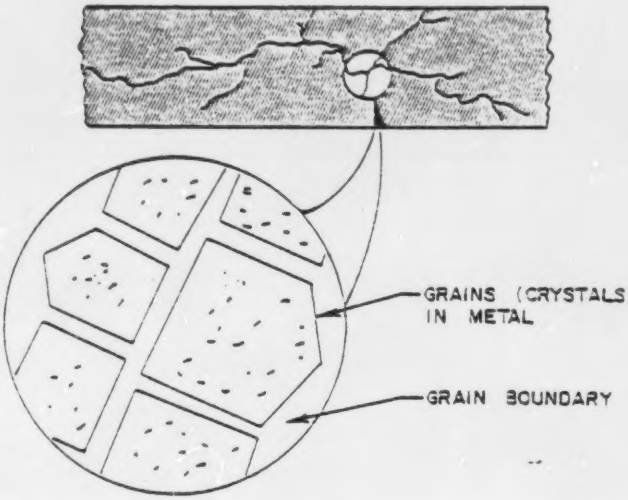


Figure 13-3-5. Intergranular corrosion.

Long corrosion cracks (top figure) along the grain boundaries may not cause much mass of metal to oxidize, but may allow cracked pieces to fail structurally when stressed.

Stainless steels, commonly used in reactor systems, if not cooled rapidly after welding, are subject to intergranular corrosion. A common method of controlling this problem is to specify alloys of low carbon content for welding application (e.g., 304 L stainless steel - the L stands for "low carbon" content).

Stress-Corrosion Cracking

Stress-corrosion cracking is generally considered to be the most serious type of corrosion because it can lead to catastrophic metal failure with little warning. For this type of corrosion to occur, three factors must be present simultaneously in neutral solutions:

Stress (forces on the metal).

Oxygen dissolved in the corrosive solution.

Dissolved ions (e.g., chloride or hydroxide ions).

Tiny cracks (fissures) begin and continue to grow in the metal along the grain boundaries. Stresses accelerate the intergranular corrosion mechanism. Very high stress on the metal can cause the metal grains to crack. In fact, increasing any of the three factors listed above is apt to accelerate the corrosion rate.

Only small amounts of oxygen and chloride (Figure 13-3-6) are necessary for stress-corrosion cracking to occur. Under normal conditions of reactor operation, oxygen and chloride levels are no greater than 0.1 ppm, corresponding to a location in the left lower corner (of the diagram) at point "X," chloride content of the water is about 10 times too high, and oxygen level is 100 times too high. Normally, the operator is warned of such potentially dangerous operating conditions by special water properties sensors (described in Module 13-5, "Water Properties Sensing").

Stress-corrosion cracking also occurs because of local hydroxide ion concentrations. Reactor water systems, at operating temperatures and pressures, have a neutral or slightly alkaline pH (i.e., they may have an excess of hydroxide ions). In crevices, or in the splash zone above the water line of a BWR or steam generator, dissolved hydroxide ions concentrate by evaporation. Dissolved oxygen is not required for failure to occur; however, if present, it accelerates cracking.

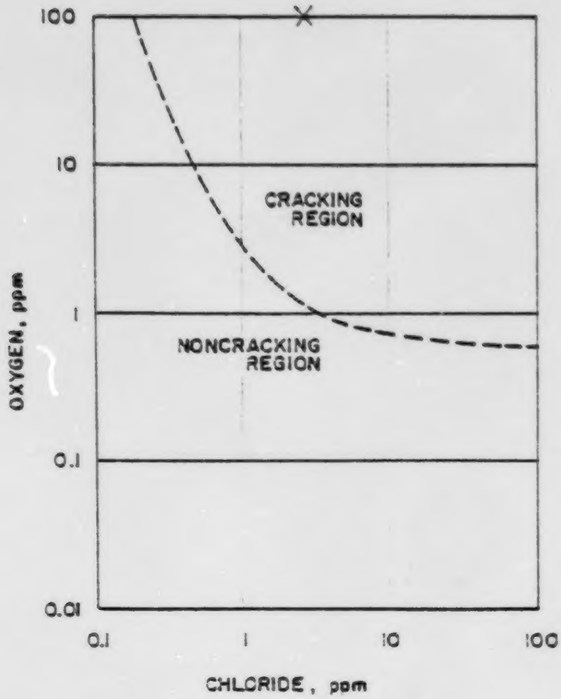
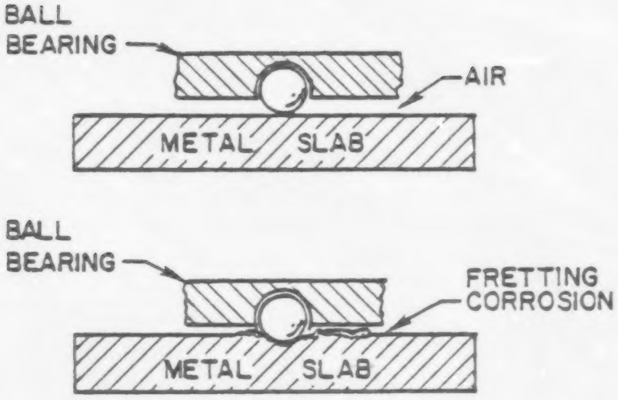


Figure 13-3-6. Relationship of chloride and oxygen content to stress-corrosion.

MECHANICAL ATTACK ON REACTOR METALS

Mechanical corrosion processes include fretting and erosion. Fretting occurs when two metal surfaces are pressed together and then subjected to vibration or slight relative motion. Oxygen must be present for damage to occur. Surfaces of ball bearings, couplings and electrical contacts are subject to this type of corrosion. Deep depressions may form and can lead to stress failure. Fretting corrosion is characterized by oxide debris, depressions or surface discoloration (Figure 13-3-7).

Figure 13-3-7.
Fretting corrosion.



Erosion occurs when particles in a liquid impinge on a metal surface, causing the wearing away of its protective surface film (Figure 13-3-8). Exposed surfaces of stainless

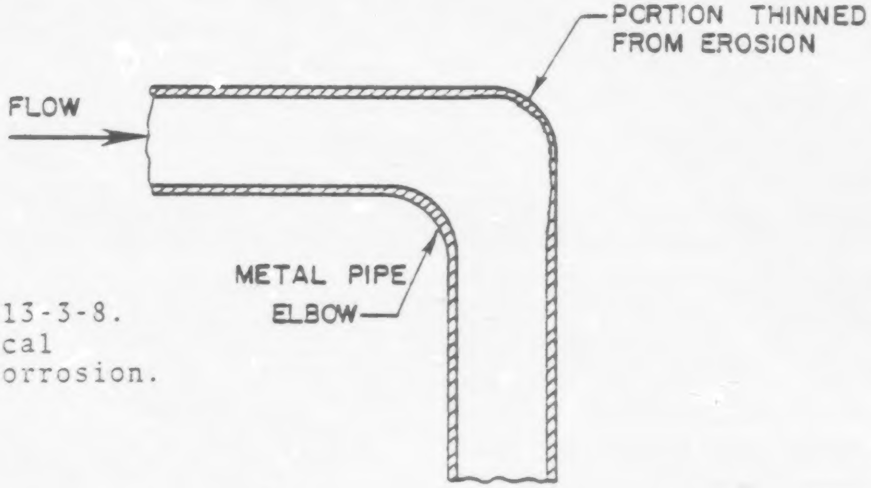


Figure 13-3-8.
Typical
erosion-corrosion.

steels, common in a PWR, erode rapidly when subjected to poor water quality.

Cavitation is the most severe form of erosion-corrosion (Figure 13-3-9). When a solid object, such as a pump impeller, moves rapidly through a liquid medium, small bubbles are formed by the low-pressure area associated with the moving object. When each bubble collapses onto the metal surface, a tiny jet of high velocity water squirts against the metal surface. Collectively, jets can penetrate the protective oxide film on a surface and even remove pieces of metal. Cavitation is often seen on pump blades. The problem may be corrected by using a harder metal in blade tips, or by changing operating conditions.

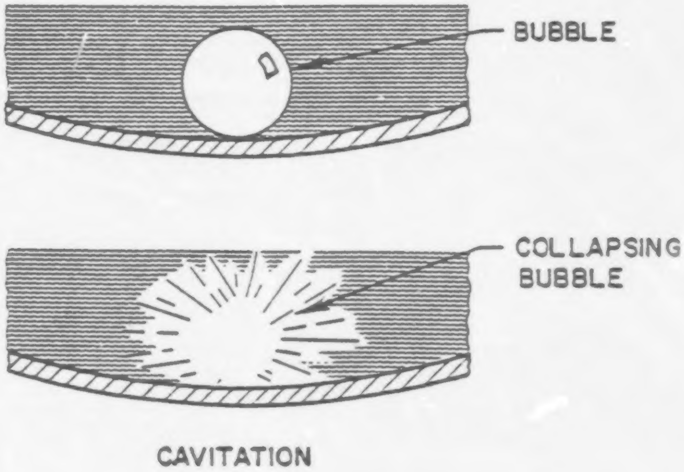


Figure 13-3-9. Typical cavitation corrosion.

SOURCES OF REACTOR IMPURITIES - METAL CORROSION

Major objectives of corrosion control in a nuclear reactor include:

Preventing metal failure (especially by stress-corrosion cracking), which could lead to a release of radioactive liquid or gas.

Minimizing exposure of operating personnel to radioactivity accumulated on metal surfaces of reactor.

Preventing buildup of radioactive corrosion products on reactor internal surfaces.

The major source of corrosion products in a nuclear power reactor is reactor metals. Because metals conduct heat readily and, when thick enough, resist tremendous pressures, reactors use various types on a variety of applications:

As heat-transfer surfaces in fuel cladding or in heater tubes (such as feedwater heaters (BWR), steam generator tubes (PWR) and condenser tubing).

As cladding (coating) for pressure vessels and system piping.

In mechanical components, such as pumps, valves and control mechanisms.

In structural components (to withstand the high steam pressures - 1000 psig to 2250 psig - such as core barrels, thermal shields and pressure vessels).

Both BWR's (Figure 13-3-10) and PWR's (Figure 13-3-11) use similar metallic components for pressure vessels, fuel rods and coolant pumps. Piping in a BWR is mostly carbon steel (except feedwater heater tubes), while piping in a PWR is stainless steel (generally of the 304 or 316 series). These metals are different because each reactor contains water solutions with different corrosive properties.

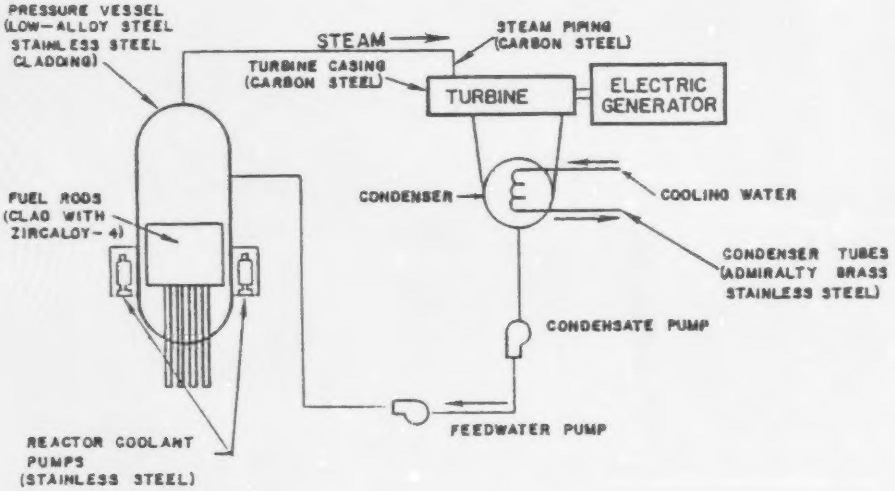

PRESSURE VESSEL (LOW—ALLOY STEEL STAINLESS STEEL CLADDING)
STEAM
STEAM PIPING (CARBON STEEL)
TURBINE CASING (CARBON STEEL)
TURBINE
ELECTRIC GENERATOR
FUEL RODS (CLAD WITH ZIRCALOY- 4)
CONDENSER
COOLING WATER
CONDENSER TUBES (ADMIRALTY BRASS STAINLESS STEEL)
CONDENSATE PUMP
FEEDWATER PUMP
REACTOR COOLANT PUMPS (STAINLESS STEEL)

Figure 13-3-10. Commonly used metals (BWR).

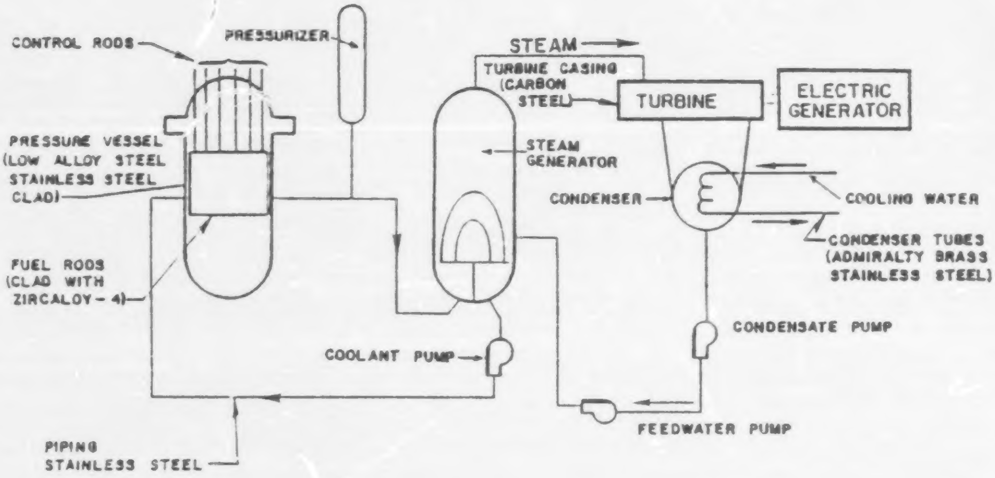

CONTROL RODS
PRESSURIZER
STEAM
TURBINE CASING (CARBON STEEL)
TURBINE
ELECTRIC GENERATOR
PRESSURE VESSEL (LOW ALLOY STEEL STAINLESS STEEL CLAD)
STEAM GENERATOR
CONDENSER
COOLING WATER
CONDENSER TUBES (ADMIRALTY BRASS STAINLESS STEEL)
FUEL RODS (CLAD WITH ZIRCALOY- 4)
CONDENSATE PUMP
COOLANT PUMP
FEEDWATER PUMP
PIPING STAINLESS STEEL

Figure 13-3-11. Commonly used metals (primary system, PWR).

CORROSION MECHANISMS FOR REACTOR METALS

The mechanism proposed in this section for rusting an iron rail is characteristic of the way corrosive solutions in coolant can affect other metals in a reactor system. Iron is selected for this discussion primarily because carbon and stainless steels (which constitute much of the reactor surface areas exposed to the corrosive environments) contain iron.

At the operating temperatures of a PWR (or BWR), iron in reactor steels reacts with cooling water as follows:

$$3Fe + 4H_2O \rightarrow Fe_3O_4\downarrow + 4H_2\uparrow.$$

Equation 13-3-1
(Equation = Eq.)

This reaction produces an insoluble coating (or film) of oxidized metal that protects the "raw," unreacted metal underneath. This surface is said to be passive. A common example of passive surface is an aluminum can covered with a thin layer of aluminum oxide (which does not corrode); however, if this surface film is scratched, the raw metal beneath reacts immediately with oxygen contained in water (or air).

Consider the corrosion of an "iron" rail in neutral (or slightly basic) water solutions (Figure 13-3-12). Water molecules continually bombard the rail surface with hydrogen and/or hydroxide ions. At the anode, metallic iron reacts with hydroxide ions and water molecules to form magnetite (Fe_3O_4). This oxide, which is highly insoluble and black, coats the rail surface when the reaction is carried out at temperatures found in the reactor circulating water (500 to 600°F). When the iron dissolves, it re-

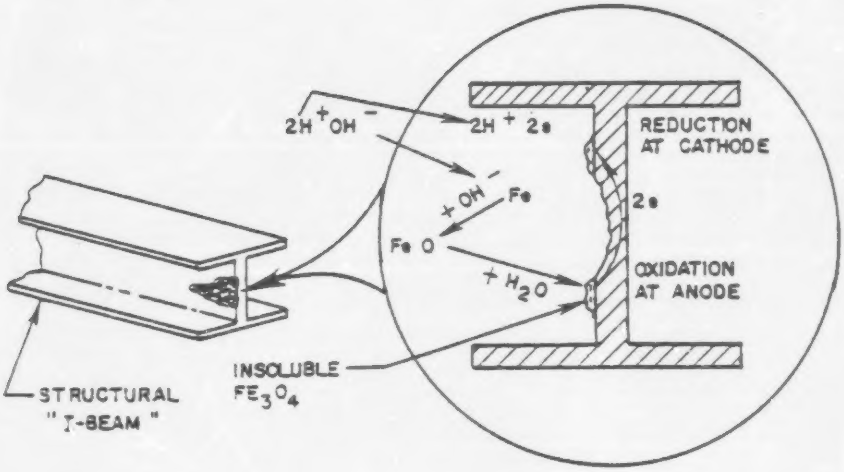


Figure 13-3-12. Corrosion of iron in neutral (or slightly basic) water solution.

releases electrons, and these electrons flow through the metal until they contact a hydrogen ion, forming hydrogen gas at a cathode site. These cathode locations may be anywhere in the metal, but the anode locations are always visible in the colored oxide films. The chemical corrosion reactions may be stated as follows:

At cathode: $2e^- + 2H^+ \rightarrow H_2$ (gas).

At anode: $Fe + 2OH^- \rightarrow FeO + H_2O + 2e.$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2.$$

Overall reaction: $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2\uparrow.$ Eq. 13-3-2

At ambient temperatures, instead of black oxide, brown $Fe(OH)_3$ is formed.

Corrosion is, therefore, an electro-chemical process with internal current flow much like that occuring in an automobile battery, but on a much smaller scale.

Accumulation of hydrogen gas, or rust, at the electrodes causes a "battery" to run down - a phenomenon called polarization. If oxygen is present at a cathode, it may react with the hydrogen gas to coat the cathode, which allows fresh hydrogen ions to reach the surface and start the oxidation reaction again.

CORROSION REDUCTION IN REACTOR METALS

Once the mechanisms that produce corrosion are understood, methods of controlling corrosion in reactor metals may be devised. A major concern in selecting reactor metals is composition of the water that will be in contact with them.

Table 13-3-2 shows the concentrations or chemicals in water, used in PWR's and BWR's. From this table, an architect-engineer selects metals relatively unreactive toward hydrogen and oxygen gases, chloride ions and fluoride ions. Lithium hydroxide and boron, in the form of boric acid, tend to neutralize each other.

TABLE 13-3-2

PRIMARY COOLANT CHEMICAL COMPOSITIONS (APPROXIMATE) FOR OPERATING LWR*

CHEMICAL FORM	BWR	PWR
Dissolved O_2 ($cm^3/kg\ H_2O$)	0.2	---
Dissolved H_2 ($cm^3/kg\ H_2O$)	0.4	25
pH (at operating temperature)	neutral	neutral
LiOH as ppm of ^7Li	---	0.5 - 2
Boron (ppm, begin of life)	---	2270
Chloride (or fluoride) (ppm)	<0.1	<0.1

SELECTION OF REACTOR PIPING AND CLADDING - STEELS

In a BWR, carbon steel is used because, at a neutral (or slightly basic) pH, its corrosion rate in water is at a minimum (Figure 13-3-13), and because it provides structural strength at the high pressures (around 1000 psig) involved.

Radiation reacts with water to produce dissolved oxygen gas in the water (Table 13-3-2). This oxygen produces negligible uniform corrosion and stress-corrosion cracking of carbon steel, as previously discussed.

In a PWR, series 300 stainless steels are used for reactor piping and cladding. Stainless steel resists the weak acidity, which sometimes exists in the coolant because the

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*LWR (light-water reactor), includes BWR and PWR.

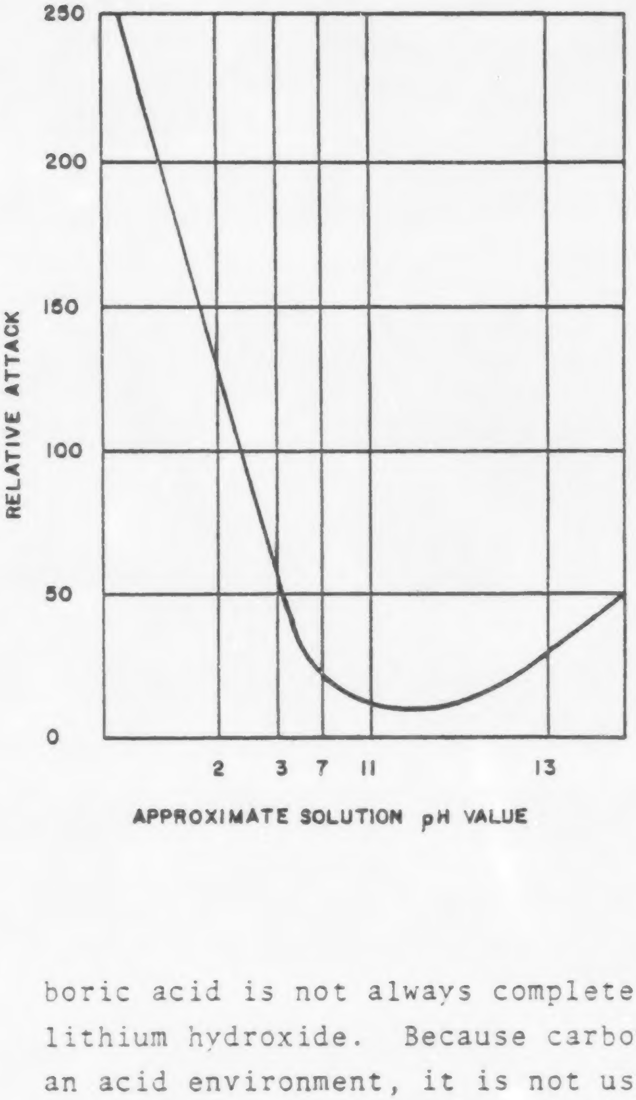


Figure 13-3-13. Relative corrosion of carbon steel as a function of pH at 590°F (310°C).

boric acid is not always completely neutralized by the lithium hydroxide. Because carbon steel corrodes rapidly in an acid environment, it is not used in PWR's.

Unfortunately, although stainless steels adequately resist changing basicity of water, they are subject to stress-corrosion cracking. Hydrogen gas is added to maintain oxygen levels at negligible values. At some time during reactor operation, because of air leakage (usually at the charging pump), dissolved oxygen levels may rise. Because stress-corrosion cracking requires not only oxygen, but also chloride ions and stress, chloride ions must be controlled to values below 0.1 ppm.

PWR STEAM GENERATOR METAL SELECTION

Metal in the tubes of a PWR steam generator is bathed in corrosive solutions from both the primary and the secondary sides of the reactor. The metal frequently selected for these tubes is Inconel-600 (about 72% nickel, with the remainder being mostly chromium and iron). This nickel-alloy may also be used as cladding for PWR reactor vessels.

On the primary side, oxygen content is reduced to negligible proportions by dissolved hydrogen gas. Inconel-600 resists corrosion about as well as 300 series stainless steels (at reactor temperatures), but it is not cracked by stress-corrosion (with chloride ions present) as are the stainless steels mentioned above. Inconel exhibits stress-corrosion cracking within high concentrations of dissolved oxygen or with caustic (hydroxide) solutions; thus, pH control is quite important. Inconel-600 is also sensitive to several ppm of lead, which can lead to cracking.

On the secondary side, Inconel tubes in the steam generator (PWR) may possibly be bathed in seawater, due to leaks in condenser tubes. Another source of corrosive impurities could be poor quality make-up water, in either the primary or the secondary systems of the reactor.

FUEL-ROD CLADDING METALS SELECTION

Zirconium alloys are most frequently selected for fuel cladding (both PWR and BWR). They have high resistance to stress-corrosion cracking and oxidation at high temperatures, and they possess good mechanical strength under operating conditions of reactor primary water systems.

Zirconium alloys can react with water to produce hydrogen:

$$Zr + 2H_2O \rightarrow ZrO_2\downarrow + 2H_2. \qquad \text{Eq. 13-3-3}$$

This hydrogen dissolves (or reacts) in metal to form platelets of $ZrH_{1.5}$ if oxidation is allowed to proceed too far.

Zirconium cladding corrodes in either fluoride or hydroxide solutions. The rate of oxidation depends upon pH (Figure 13-3-14). This graph shows the number of days to reach a given thickness of corrosion layer (in mg/dm^2) as the pH of the water solution varies at the approximate operating temperature of a reactor. For example, at pH 13, only 30 days are required to reach 35 mg/dm^2; 200 days are required to form 500 mg/dm^2 of ZrO_2.

Because lithium hydroxide solutions are used in a PWR to neutralize boric acid (neutron poison), careful control of its concentration is necessary to prevent breaching of the fuel cladding.

Zirconium also reacts with fluoride ions, thus its concentration must be regulated below 0.1 ppm by careful control of the make-up water and by purification of the circulating coolant water.

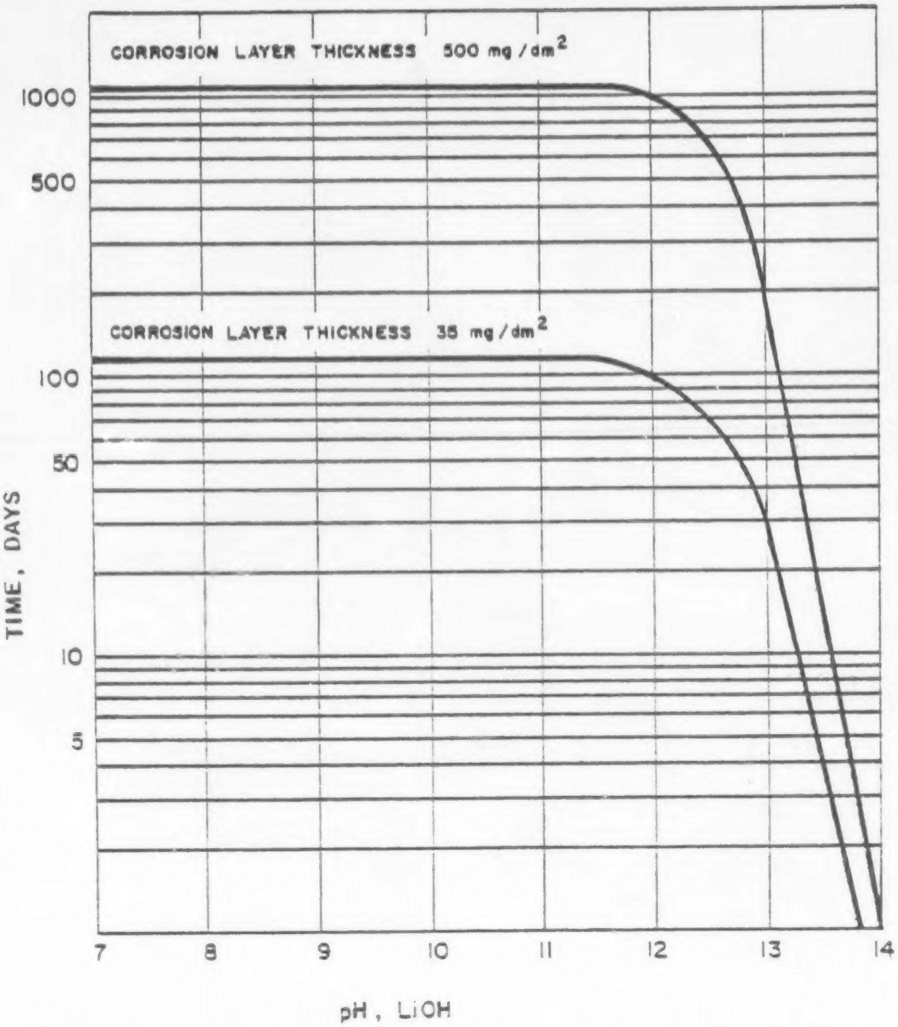


Figure 13-3-14. Corrosion-layer buildup for zirconium.

CONDENSER TUBE METAL SELECTION

Condenser tubes are immersed in two corrosive solutions and must be carefully selected for resistance to dissolved materials in both. In a BWR, one side of the condenser is exposed to "pure" water on the primary side of the reactor at several hundred degrees Fahrenheit; on the other side, the tubes are exposed to low-quality water at ambient temperature. In a PWR, one side of the condenser is exposed to the nearly "pure" water of the secondary system; on the other side, the tubes are exposed to low-quality water at ambient temperatures. Since this low quality water may be obtained from the ocean, lakes or rivers, its quality will vary more widely than any water used in the reactor system.

SOURCES OF REACTOR IMPURITIES - ACTIVATION PRODUCTS

Chemicals dissolved or suspended in primary reactor coolant by corrosion mechanisms react with thermal neutrons as they circulate through a reactor core. These reacting nuclides may have originally been part of the reactor structural metals, or gases that leaked into the system from the atmosphere, or dissolved ions in the make-up water. Table 13-3-3 lists some common activation products in reactor primary systems.

TABLE 13-3-3
TYPICAL ACTIVATION PRODUCTS

NUCLIDE	HALF-LIFE	REACTION	MAJOR SOURCE
^{3}H	12.26 y	^{10}B(n,2α)^{3}H	Boron in Coolant
		^{6}Li(n,α)^{3}H	Lithium in Coolant
^{16}N	7.1 s	^{16}O(n,p)^{16}N	Water
^{17}N	4.14 s	^{17}O(n,p)^{17}N	Water
^{18}F	110 min	^{18}O(p,n)^{18}F	Water
^{13}N	9.96 min	^{16}O(pα)^{13}N	Water
^{24}Na	5 h	^{23}Na(n,γ)^{24}Na	Impurity in Water
^{41}Ar	1.83 h	^{40}Ar(n,γ)^{41}Ar	Air in Water
* ^{51}Cr	27.8 d	^{50}Cr(n,γ)^{51}Cr	Steel and Inconel
* ^{54}Mn	312 d	^{54}Fe(n,p)^{54}Mn	Steel and Inconel
* ^{59}Fe	45 d	^{58}Fe(n,γ)^{59}Fe	Steel and Inconel
* ^{58}Co	71 d	^{58}Ni(n,p)^{58}Co	Nickel alloys
* ^{60}Co	5.24 y	^{59}Co(n,γ)^{60}Co	Trace in Nickel Alloys & Stellite
^{64}Cu	12.9 h	^{63}Cu(n,γ)^{64}Cu	17-4 PH Steel
^{95}Zr	65 d	^{94}Zr(n,γ)^{95}Zr	Zircaloy
^{181}W	130 d	^{180}W(n,γ)^{181}W	Steel, Carbides
^{187}W	24 h	^{186}W(n,γ)^{187}W	Steel, Carbides

* Activation Products of Major Concern

ACTIVATION PRODUCTS OF MAJOR CONCERN

The operator of a nuclear power plant is concerned mainly with those corrosion products with long half-life and those that emit penetrating gamma rays. In Table 13-3-3, these products of major concern are marked with an asterisk. They are generated mainly from the corrosion products of the steels and Inconel used in reactor piping and cladding.

INSOLUBLE SOLID ACTIVATION PRODUCTS -CRUD

Radioactive, metal-oxide, solid corrosion products, suspended in the reactor coolant or appearing as a film on reactor surfaces, are called crud. These crud particles range (roughly) from 0.01 and 0.5 micrometers in diameter (1/250,000 - 1/51,000 inch). Chemical composition of crud depends upon relative corrosion rates and quantities of corroding metal. For typical values, refer to Table 13-3-4.

TABLE 13-3-4
SAMPLE COMPOSITIONS OF CRUD IN LW REACTORS (W/O)

	% Fe	% Ni	% Cr	% Co	% O
PWR	60	5	3	0	32
BWR	65	-	-	8	27

The iron appears mainly in the form of insoluble Fe_3O_4 (black magnetic oxide) in both PWR's and BWR's. Insoluble nickel or chromium oxides are present in a PWR because of stainless steel and Inconel (both contain these elements). Copper, in a BWR, is due to the corrosion of admiralty brass (from condenser tubes).

The "crud cycle" in reactor coolant redistributes radioactive crud from the reactor core to other parts out-of-core by two mechanisms. In the first, a steady-state mechanism (Figure 13-3-15), MeO represents metal oxide corrosion product; MeO* represents activated metal oxide. This deposition of crud occurs preferentially in low velocity areas- (e.g., at heat exchanger heads, pump volutes and check valves) with a half-life of about 30 minutes.

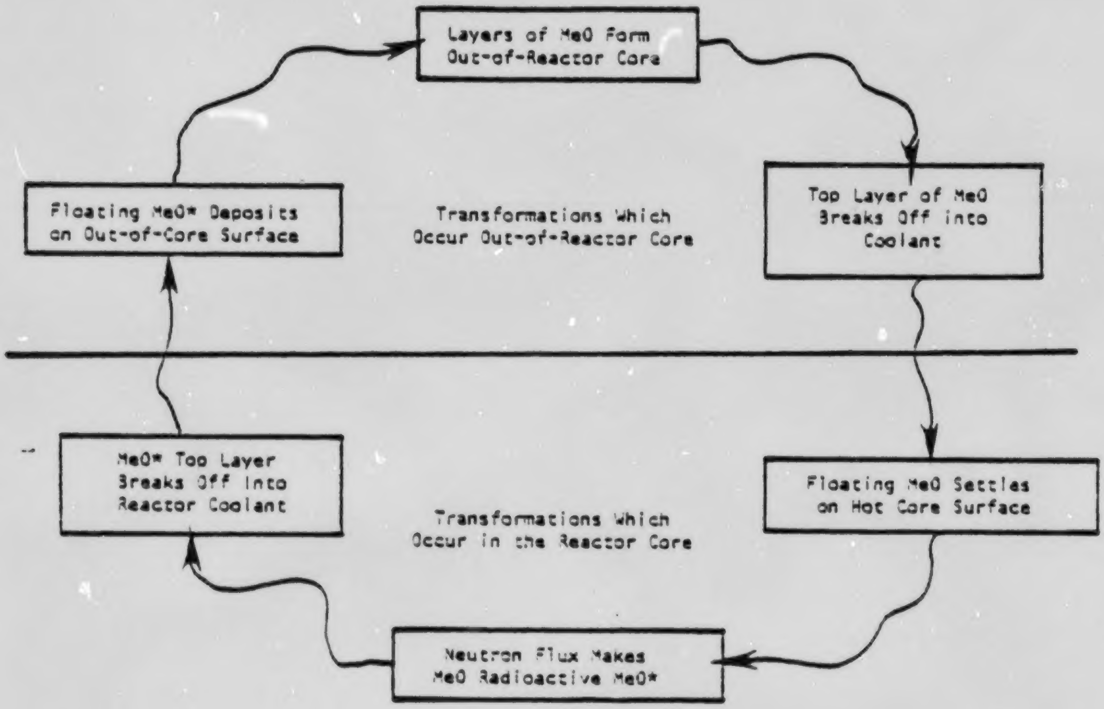

Layers of MeO Form Out-of-Reactor Core
Top Layer of MeO Breaks Off into Coolant
Floating MeO* Deposits on Out-of-Core Surface
Transformations Which Occur Out-of-Reactor Core
MeO* Top Layer Breaks Off Into Reactor Coolant
Floating MeO Settles on Hot Core Surface
Transformations Which Occur in the Reactor Core
Neutron Flux Makes MeO Radioactive MeO*

Figure 13-3-15. Mechanism for transport of crud from one part of reactor to another - "crud cycle."

The second mechanism, "crud burst," consists of a flood of corrosion products shaken loose from one part of the system and transiently injected into the primary coolant system. The crud is ultimately removed by deposition on reactor surfaces or by filtration in the demineralizers. Disturbances which produce crud bursts include rapidly changing flow rates and temperatures (such as occur during start-up or shutdown), mechanical shock (such as is experienced in a "scram") and chemical shock.

SOURCES OF REACTOR IMPURITIES - FISSION PRODUCTS

Two other common sources of radionuclides found in reactor primary coolant systems are 1) "tramp" uranium and 2) leaks in cracked fuel pellets.

"TRAMP" URANIUM

Tramp.uranium is carried into the reactor from the fuel fabrication plant as a surface impurity or as an impurity in the welds (0.1 to 1 ppm of uranium). Thermal neutrons fission all the tramp uranium; however, only those fission products within the 7-to 11-micron range enter the coolant. Fragments formed at greater distances interact with the metal before release into the coolant. What is shown (Figure 13-3-16) for radioiodine is also typical of other fission products, with a different time scale for each product.

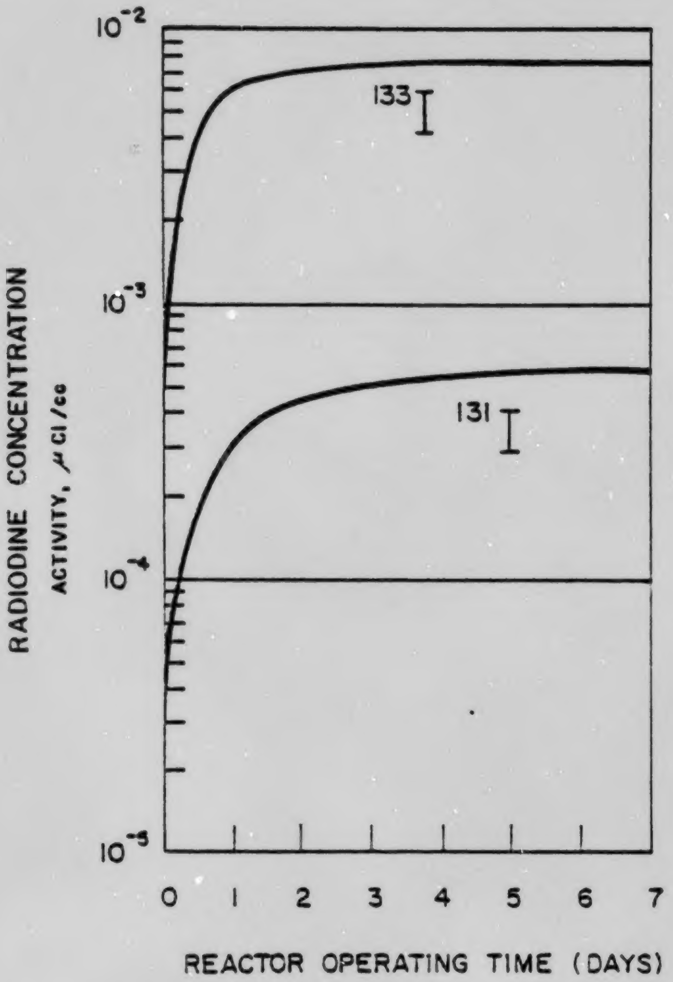


Figure 13-3-16. Gross radioiodine expected in reactor coolant from surface contamination of fuel elements.

LEAKS FROM CRACKED FUEL ELEMENTS

Although over 200 radionuclides can be identified in coolant (due to leakage of fission products from cracked fuel), only those shown in Table 13-3-5 leak from the fuel in significant amounts. Observe that these fall into three groups:

Gaseous (including Xe, Kr, bromine and iodine).
Dissolved ions (including Ca, Sr, Y, Ba and Ce).
Tritium.

TABLE 13-3-5

FISSION PRODUCTS FOUND IN THE REACTOR COOLANT IN SIGNIFICANT AMOUNTS

Isotope	Half-Life
^{84}Br	31.8 mins
$^{85}Kr^m$	4.4 hrs
^{85}Kr	10.74 yrs
^{87}Kr	76.0 mins
^{88}Kr	2.79 hrs
^{88}Rb	17.7 mins
^{89}Rb	15.2 mins
^{89}Sr	50.8 days
^{90}Sr	28.9 yrs
^{91}Sr	9.67 hrs
^{92}Sr	2.69 hrs
^{90}Y	64.0 hrs
^{91}Y	58.8 days
^{92}Y	2.69 hrs
^{99}Mo	66.6 hrs
^{131}I	8.065 days
^{132}I	2.284 hrs
^{133}I	20.8 hrs
^{134}I	52.3 mins
^{135}I	6.7 hrs
$^{131}Xe^m$	11.96 hrs
$^{133}Xe^m$	2.26 days
^{133}Xe	5.27 days
$^{135}Xe^m$	15.7 mins
^{135}Xe	9.16 hrs
^{138}Xe	14.2 mins
^{134}Cs	2.60 yrs
^{136}Cs	13.0 days
^{137}Cs	30.2 yrs
^{138}Cs	32.2 mins
^{139}Ba	84.0 mins
^{140}Ba	12.8 days
^{140}La	40.23 hrs
^{144}Ce	284.4 days

Tritium, a radioactive isotope of hydrogen, decays by an 18.6 keV beta particle and has a half-life of 12.33 years. Because its beta-emission energy is very low, tritium does not generally create significant external radiation problems; however, it can enter the body by ingestion, inhalation or absorption through the skin. Once inside the body, it combines chemically as hydrogen, and the He-3 resulting from tritium beta decay can cause cell damage by breaking the hydrogen chemical bond.

Tritium can be produced either by terniary fission of U-235 (and subsequently diffuse through the intact Zircaloy-4 cladding to the reactor coolant) or by neutron reactions with species present in the coolant. Only a small fraction (approximately 1%) of the total tritium produced in the fuel diffuses through the cladding. The larger portion of the tritium is retained in the cladding by chemical hydriding reactions with the zirconium. The predominate sources of tritium by neutron reactions include:

REACTION	THRESHOLD
$^{10}B(n, 2\alpha)T$	1 MeV
$^{10}B(n,\alpha)^{7}Li(n,n\alpha)T$	Thermal; 3 MeV

Since the Li-6 is minimized in the primary coolant, the first two B-10 reactions and the Li-7 reaction are the predominant sources of tritium. B-10 is also used as a liquid poison in PWR's and in control rods in BWR's. Li-7 is used in PWR's for pH adjustment. From an operations viewpoint, tritium buildup is undesirable because maintenance personnel must wear air-supplied plastic suits to prevent absorption through pores of the skin.

EXERCISES

1. A reactor operator is notified by the plant chemist that Na-24 concentration in the hotwell measures 1500 dpm/milliliter and Na-24 concentration in the primary coolant is 1/5 microcuries/milliliter. What is the best estimate of the percent carryover?
2. In a circulating reactor coolant, calcium sulfate hardness is reduced each hour from 1.0 ppm to 10 ppb by retention of the demineralizers. If coolant flow is 68 million kilograms per hour, how many pounds of calcium ion are removed hourly?
3. Use Figure 13-3-14; calculate corrosion rate of Zircaloy-4 at pH 10 in both mg/dm^2/mo and pounds/ ft^2/ year.
4. If condenser tubes on a BWR leak small amounts of seawater, air gets into the circulating coolant. If these are not removed by the purification system, what type of corrosion would eventually occur in the feedwater heater tubes?
5. If the uniform corrosion rate of stainless steel piping in a PWR is 10 mg/dm^2/mo, what is thickness of metal lost in mils/year and in millimeters/years?

MATERIALS

1 tank or lecture bottle of oxygen.

1 tank or lecture bottle of nitrogen.

2 500-ml Erlenmeyer flasks.

2 10-inch lengths of 6-8 mm glass tubing.

Suitable lengths of rubber tubing.

Distilled water, previously de-aerated by boiling.

Mineral spirits of benzene.

Acetone.

Iron turnings.

1 piece of carbon steel sheet of convenient size (e.g., 2" x 8").

1 piece of 3% chromium steel.

1 piece of 6% chromium steel.

1 piece of 12% chromium steel.

1 piece of 18% chromium, 12% nickel steel.

1 beaker, 600 ml.

10% copper sulfate solution.

2 strips 18-8 (series 300) chromium-nickel stainless steel, 1-1/2" x 1-1/2" x 6" (approximately).

1 strip carbon steel, 1-1/2" x 6".

1 strip of platinum sheet or foil.

Sulfuric acid, concentrated.

Nitric acid, concentrated.

Distilled water.

Millivoltmeter, 0-1000 mv d.c.

Wires and suitable clips to connect samples to millivoltmeter.

1 1000 ml beaker.

1 250 ml beaker.

1. Demonstrate importance of oxygen in the corrosion of iron in water. (Caution - review safety rules associated with use of oxygen.)
   a. Pour 250 ml distilled water into each of the 500-ml Erlenmeyer flasks.
   b. Use the lengths of glass tubing as bubblers; connect one to a source of nitrogen and allow it to bubble through distilled water in one flask.
   c. Similarly, allow oxygen to bubble through distilled water in second flask.
   d. Degrease iron turnings by rinsing first with benzene or mineral spirits and then with acetone.
   e. After rapid drying, preferably in a stream of clean air, weigh two 50-gram samples and introduce them into flasks containing distilled water.
   f. Continue to bubble gases through flasks.
   g. Enter results on Data Table 13-3-1.
2. Demonstrate passivation of steel by alloying it with chromium or chromium and nickel (galvanic series).
   a. Immerse, successively, in copper sulfate solution, the five metals listed on Data Table 13-3-2.
   b. Re-immerse metals in copper sulfate; remove them and tap each one with a glass rod.
3. Demonstrate active and passive electrode potentials of stainless steel.
   a. Pour approximately 600 ml of distilled water into a 1000-ml beaker; add, slowly and carefully with constant stirring, 150 ml of concentrated sulfuric acid. (Caution: This mixing generates considerable heat and must be done with great care.) While dilute acid is still hot, suspend in acid - so

that they do not touch each other - one strip of carbon steel and one of 18-8 (series 300) stainless steel. Connect them to millivoltmeter; note and record voltage on Data Table 13-3-3.

b. Without removing either specimen from the acid and without disconnecting them from the voltmeter, bring the carbon steel into contact with the stainless steel below the surface of the acid.

c. Separate the carbon steel from the stainless steel and remeasure voltage.

d. Replace carbon steel with a new (passive) piece of stainless steel.

e. Connect to millivoltmeter.

f. Add 150 ml of concentrated nitric acid to sulfuric acid (after completing d and e); note potential between active and passive samples of stainless steel.

g. Enter all results on Data Table 13-3-3.

DATA TABLE 13-3-1

As oxygen and nitrogen gases bubble through the solutions, observe changes(s) if any, in iron turnings.

TIME ELAPSED (min)	CHANGES OBSERVED IN FLASKS	
	Containing O_2	Containing N_2
0		
30		
60		
90		
120		
150		
180		

DATA TABLE 13-3-2

Record how rapidly the copper plates - out on the listed metals. (Note: Copper is in the center of Table 13-3-1. It should plate out MORE RAPIDLY on those metals above it in the Galvanic Series than those below it.)

1.

METAL IMMERSED	RATE OF COLORATION (fast, moderate, slow, none)
Carbon Steel	
3% Chromium Steel	
6% Chromium Steel	
12% Chromium Steel	
18-8 Cr-No Steel	

2. What is effect of tapping on the 12% chromium steel?

3. Will mechanical shock destroy the passivity of series 300 (18-8) chromium-nickel steel? ____________
Why?

DATA TABLE 13-3-3

1. Millivoltmeter reading: ____________ ______mv

2. What gas is evolved in step b of the Procedures?

____

Why? ____

____

3. After step b, the stainless steel is no longer "passive," as shown in Table 13-3-1. Record new millivoltmeter reading: ________________________ mv

4. Remeasure voltage after replacing carbon steel, as in step d. How does it compare with value in step a?

____ mv

Why? ____

____

5. After adding nitric acid (Procedure, step f), observe potential between two stainless steel electrodes. Why has the __________ mv potential changed?

____

____

REFERENCE MATERIALS

Krugers, J., ed. Instrumentation in Applied Nuclear Chemistry. New York: Plenum Press, 1973.

Semat, H. and Albright, J.R. Introduction to Atomic and Nuclear Physics. 5th ed. New York: Holt, Rinehart and Winston, 1972.

TEST

1. Define or describe:

   Boiler scale.

   Steam carryover.

   Corrosion.

   Activation products.

   Crud.

2. List the two most common methods used to reduce boiler scale:

   (1)

   (2)

3. Briefly describe carryover and why this may be a significant problem in power plant steam generators:

4. List methods used to reduce steam carryover:

5. Briefly explain the following types of corrosion:
   Erosion.

   Uniform.

   Galvanic.

Crevice.

Pitting.

Intergranular.

Stress-corrosion cracking.

Fretting.

Cavitation.

6. List and explain the four major objectives for control of corrosion in a nuclear reactor:

(1)

(2)

(3)

(4)

7. Briefly describe mechanisms for corrosion in reactor materials:

8. Briefly describe the two most important methods used to reduce corrosion in reactor materials at the design stage:

9. List three major sources of activation products in the reactor coolant:

10. List the range of particle sizes and composition of typical crud:

11. Briefly describe the mechanisms for release and transport of radioactive substances within a coolant:

12. Briefly describe mechanisms for accumulation of fission products in reactor coolant and feedwater:

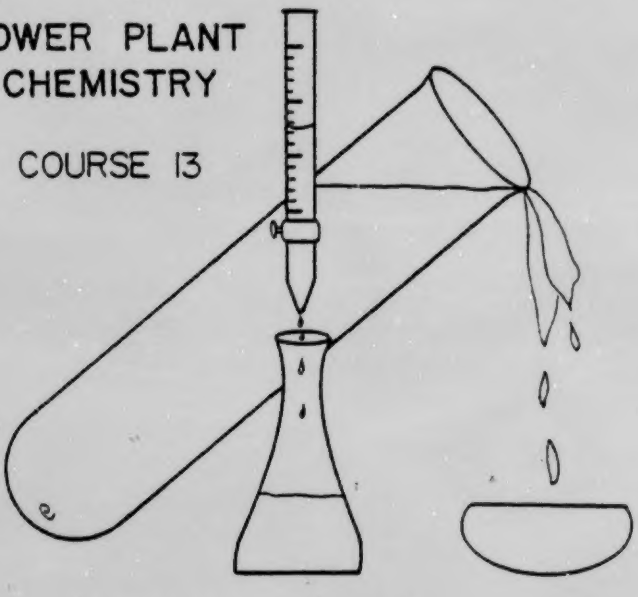
NUCLEAR TECHNOLOGY

MODULE 13-4 WATER TREATMENT - POLISHING BY ION EXCHANGE, EVAPORATION AND DEMINERALIZATION. -

ROBERT B. NEEL

POWER PLANT
CHEMISTRY

COURSE 13



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COURSE MODULES

COURSE 13 POWER PLANT CHEMISTRY

MODULE 13-1	Water Quality Control
MODULE 13-2	Raw-Water Treatment
MODULE 13-3	Sources of Impurities in Reactor Water Systems
⇨ MODULE 13-4	Water Treatment - Polishing by Ion Exchange, Eavporation and Demineralization
MODULE 13-5	Water Properties Sensing
MODULE 13-6	Water Analysis for Nuclear Power Plants
MODULE 13-7	Radioactive Waste Handling - Liquid and Gaseous

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INTRODUCTION

Water used for cooling systems in nuclear power plants must be as free of dissolved and suspended solids as modern technology can achieve. In this pure liquid, metal corrosion products accumulate slowly. These corrosion products then circulate through the reactor core region and become radioactive under neutron bombardment. Make-up water, used to replace system fluid losses, also contains trace level impurities, which accumulate in the system if not removed.

To maintain acceptable reactor cooling water quality, continuous purification is necessary. This module describes the types of systems used for this purification and the chemical principles used in their design and operation.

MODULE PREREQUISITES

The student should have completed all previous modules in this Course.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Discuss the following theories:
    - Ion exchange softening.
    - Evaporation.
    - Demineralization.
    - Pre-coat filtration.
2. Give typical values for the following design parameters for an ion exchange softening system:
    - Maximum operating temperature.
    - Exchange capacity (in equivalents per liter).
    - Moisture content.
3. Give typical values for the following design parameters for a demineralization system:
    - Maximum operating temperature.
    - Cation and anion exchange capacities of the resins (both separate and combined).
    - Flow rates through exchangers.
    - Moisture content.
4. Discuss principles involved in precoat, deep-bed and filter/demineralization filtration systems used for reactor condensate polishing.
5. Describe a purification system for PWR and BWR primary coolants.
6. Discuss when and why an evaporation system is used.
7. Set up and operate a bench scale ion-exchange system to remove impurities, hardness and acidity in water.

THE ION-EXCHANGE (SOFTENING) PROCESS

Nuclear power plants use ion-exchange methods as the principal chemical process for removal of dissolved impurities. The process is usually carried out in a steel container called an ion exchanger. From the outisde, the ion exchanger (Figure 13-4-1) appears much like an ordinary pressure filter.

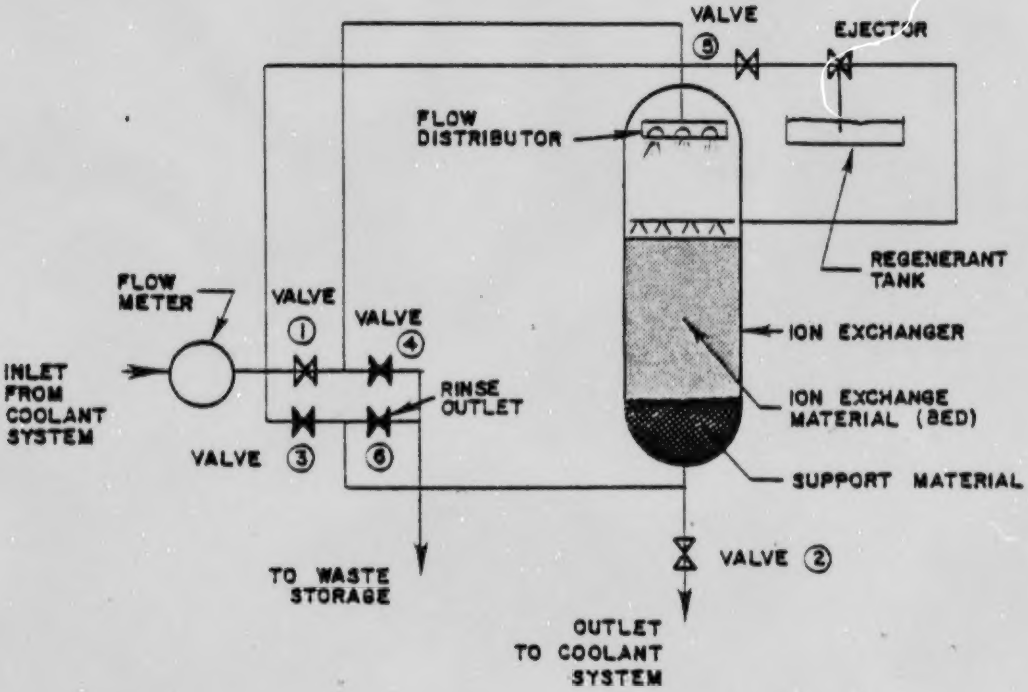


Figure 13-4-1. Typical ion-exchange unit.

During the initial purification phase, contaminated water flows into the unit through valve No. 1 and is sprayed onto the exchange material (called a bed). Dissolved ions are removed chemically, and the purified ("softened") water leaves through open valve No. 2. The filled-in (black) valve symbol should be interpreted to mean that the valve is normally closed. Other portions of the figure indicate additional plumbing used in a recycling or regeneration mode.

Two forms of ion-exchange resins are commonly used in nuclear power plants today:

Cation (strongly acid).
Anion (strongly basic).

Both are synthetic organic materials derived from styrene and benzene, and both are negligibly soluble in water solutions found in power plants. Table 13-4-1 provides a brief listing of physical and chemical properties of these two resin types.

Resin particles usually are supplied by the manufacturer in the form of spherical beads, several tenths of an inch in diameter. They are poured into a steel container and washed to remove traces of residual impurities. During washing, the beads soak up water, increasing in volume to a moisture content of about 50% by weight.

A "deep bed" of resin, several feet thick, can cause a hydraulic pressure loss of approximately 1 psi per foot of bed thickness. Contaminated water normally flows into the bed at a rate of between 3 and 10 gallons/minute for each cubic foot of bed volume.

Temperature of the contaminated water, in normal nuclear applications, is always less than 140°F (60°C), the temperature at which many resin beads begin to dissolve.

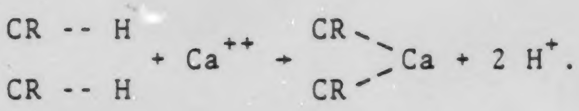
TABLE 13-4-1
APPROXIMATE PHYSICAL AND CHEMICAL PROPERTIES OF SELECTED ION-EXCHANGE RESINS (STRONG TYPE)

PROPERTY	CATION (CR)	ANION (AR)
Maximum resin size (mm/in)	0.5/0.2	0.6/0.24
Moisture (%)	60%	55%
Wet capacity (equivalents/ liter)	2	1
ΔP (psi/ft of bed)	1	1
Flow rate (gpm/ft^2)	50	17.5
(gal/ft^3/min)	10	3.5
Operating temperature in °F (°C) (maximum allowed)	250 (120)	140 (60)
Common chemical form	$R\text{-}SO_3^-\text{-}H^+$	$R\text{-}N\text{-}(CH_3)_3^+\text{-}OH^-$

In one common form of cation resin (CR), hydrogen ions are loosely bound to the exchange medium by sulfate bonds. In the common form of the anion resin (AR), the quaternary ammonium type, hydroxide ions are loosely bound.

ION-EXCHANGE THEORY

Chemical ions, which are loosely bound to the ion-exchange resin sites, may be exchanged (or replaced) by other chemical ions in solution (if those dissolved ions have a greater attraction for the resin sites than the already bound ions). For example, consider a cation resin in hydrogen form reacting with a calcium ion that produces hardness in water:



$$\begin{matrix}CR\text{ -- }H\\ CR\text{ -- }H\end{matrix} + Ca^{++} \rightarrow \begin{matrix}CR\diagdown\\ CR\diagup\end{matrix}Ca + 2\,H^{+}.$$

Equation 13-4-1
(Equation = Eq.)

Two bound hydrogen ions in the resin are displaced by the calcium ion, which has a greater affinity for the resin. For nearly pure water solutions, such as those found in reactor water systems, an ion on the left in the following series may replace any ion on the right that is bound to the cation resin:

$$Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++} > NH_4^{\ +} > Na^{+} > H^{+} > Li^{+}.$$

In Equation 13-4-1, the number of hydrogen atoms displaced is equal to the number of charges on the calcium ion. The number of charges is called the number of equivalents of an ion. Thus, two equivalents of calcium ion (2 + charges and one ion) displace two equivalents of hydrogen (2 + charges and two ions).

Anion resins can replace hydroxide ions in the resin with contaminated ions from the solution in a manner similar to the process for cation exchange. For example, consider the removal of chloride ions by a strong base anion exchanger:

$$AR\text{ -- }OH + Cl^{-} \rightarrow AR\text{ -- }Cl + OH^{-}.$$

Eq. 13-4-2

One equivalent of chloride ion displaces one equivalent of hydroxide ion into the solution. In reactor water, ions to the left (in the series below) may replace any ion to its right that is bound on the anion resin:

$$I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > OH^- > F^-.$$

Because the resin bed volume is of limited size and the capacity (eq/l) of resin is also limited, the ion exchanger unit has a finite lifetime. After a certain number of gallons of impure solution have been passed through the exchanger, all the ion-exchange sites are filled with offending ions and the bed begins to pass (or leak) additional ions - the breakthrough point. In a nuclear power plant, breakthrough is most readily detected by monitoring the ion exchanger output effluent for radioactivity.

REGENERATION OF ION-EXCHANGE RESINS

The first step in regeneration is backwash, a physical process that removes fines (tiny solid corrosion products that cling to, or are adsorbed by, the resin beads).

After fines are removed, dissolved ions may be removed by chemical regeneration. The chemicals used for regeneration are relatively concentrated solutions of acid for the cation resins (sulfuric acid) and concentrated solutions of base for the anion resins (sodium or lithium hydroxide). The following typical reactions take place during regeneration:

$$\mathrm{CR -- M + H_2SO_4 \rightarrow \begin{array}{l} CR -- H \\ CR -- H \end{array} + M_2SO_4.}$$

Eq. 13-4-3

$$\mathrm{AR -- Cl + NaOH \rightarrow AR -- OH + NaCl.}$$

Eq. 13-4-4

In Equation 13-4-3, "M" represents any metal cation. The resins, after regeneration, are returned to their original forms and the contaminant ions are discharged to the waste system.

The mechanism of the regeneration process may be better understood by referring again to Figure 13-4-1 and to Table 13-4-2. Valves 5 and 6 are opened and valves 1, 2, 3, and

TABLE 13-4-2

VALVE POSITIONS VERSUS MODE OF OPERATION

Operation	Valve Number					
	1	2	3	4	5	6
Purification	O	O	X	X	X	X
Backwash	X	X	O	O	X	X
Regeneration	X	X	X	X	O	O
Flush	O	X	X	X	X	O

O = Open X = Closed

All valves closed between different operating modes.

4 are closed. Water passes through the inlet meter, through valve 5 and through the ejector; it is then sprayed into the resin bed and leaves through the outlet valve 6. The rapid motion of this water through the ejector sucks regenerating solution from the tank into the flowing stream. This chemical solution is rinsed out of the bed by returning the system to the valve settings shown (Figure 13-4-1) and by flushing with large quantities of water. The flushing continues until the conductivity of the effluent is within the limits desired.

THE DEMINERALIZATION PROCESS

Cation and anion resins are usually physically mixed together in the steel ion-exchanger container to produce "ion-free" water. A "mixed-bed" ion exchanger (generally called a demineralizer) commonly mixes two volumes of cation ion resin to one volume of anion resin. Although separate beds of each resin (in two containers) connected in series (with pipe) could be employed, the effluent water from the mixed-bed is generally of higher quality. The ion-exchange processes described by Equations 13-4-1 and 13-4-2 proceed simultaneously in a demineralizer.

Like a single-bed ion exchanger, a mixed-bed exchanger also becomes chemically exhausted and requires chemical regeneration. When the effluent conductivity shows that the bed must be regenerated, the first step is a backwash.

Although many regenerations may be performed with the resins in place, some demineralizers are designed for regeneration out of the container used during normal operations. These resins are sluiced with water to some distance away for regeneration, and then returned to the demineralizer when chemically restored.

FILTRATION SYSTEMS FOR CONDENSATE POLISHING

On a weight basis, most of the impurities in reactor primary coolant are insoluble, radioactive metal oxides (crud). Filtration is, therefore, as important in purification of the water as is ion exchange itself. These two processes tend to complement each other; one removes insoluble solids; the other removes dissolved ions.

Three principal approaches to filtration are currently in use:

Deep-bed.
Pre-coat/cartridge.
Filter-demineralizer filtration.

Cartridge Filtration

The simplest method of the three is cartridge filtration (Figure 13-4-3). Different materials may be used in

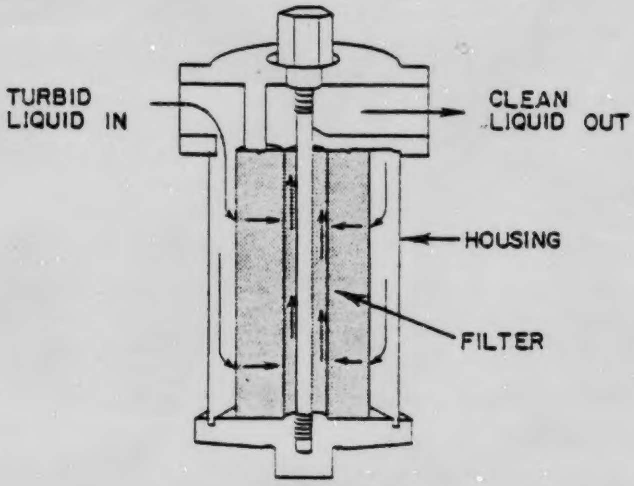


Figure 13-4-2. Typical cartridge filter.

constructing the filter media proper:

Sintered metal.

Porous ceramic.

Fiber yarn (wound around a sintered metal core).

These filters can be used alone or in combinations with others. They may vary in length from <10 to >30 inches (25 to 75 cm) and are usually several inches in diameter.

A cartridge filter is often used as a prefilter, before an ion exchanger. As a prefilter, it removes a substantial part of the insoluble corrosion products before they can cause clogging in the ion exchanger. Its filtration efficiency is greater than 90% for particles as small as 1 micron (0.04 inches). After extended usage, however, pores of the filter become clogged. A simple differential-pressure gage across the filter indicates when plugging is sufficiently serious to warrant filter replacement. The filter materials are generally highly radioactive and are disposed of as solid radwaste.

Deep-Bed Filtration

If reactor coolant is circulated rapidly enough through an ion-exchanger bed, the deep bed acts as a filter for insoluble crud itself. At velocities of 50 gal/min/ft^2 of bed, removal efficiencies of greater than 90% have been reported.

Usually, five to ten deep-bed units are used in parallel during normal operations. This filter removes more corrosion products as insoluble solids than as dissolved ions. Thus, it acts much like a mechanical filter.

Mixed-bed ion-exchange demineralizers of this type offer the advantage of a large reserve capacity for removal of dissolved solids from the coolant. This reserve capacity is particularly desirable in the condensate demineralizer, which follows the condenser. If the condenser tubes develop small leaks, raw water enters the steam generator of a PWR or the feedwater of a BWR. The large reserve exchange capacity allows the operator to make an orderly shutdown of the reactor if the leak is large, or allows continued operation if leak is small.

Pre-Coat Filtration

Pre-coat filters use pulverized (cation and anion) ion-exchange resins to form a layer (or coat) of about 0.2 pounds/square foot over a cylindrical porous ceramic or metal element (Figure 13-4-3).

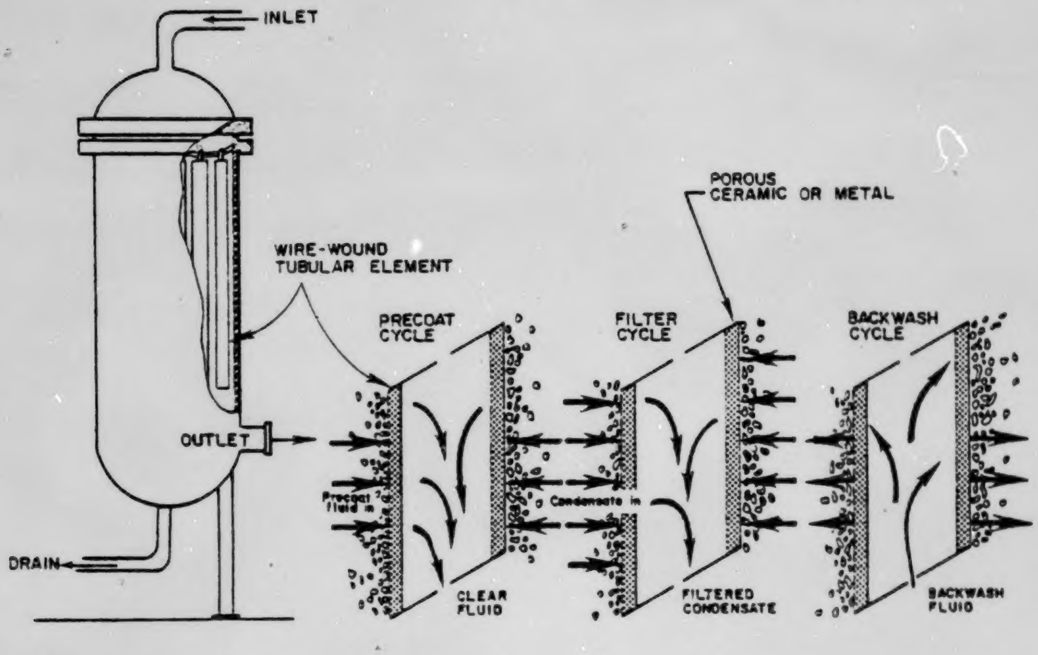


Figure 13-4-3. Typical pre-coat filter.

In a "pre-coat cycle," solution containing resin particles (400 mesh, 0.002 inches or 0.004 mm) is flushed through the filter container and deposited on the porous elements. (There are usually less than 100 of these larger elements in a filter housing.) This slurry is recirculated through the filter until it is clear in the drain, which means that all of the resin is deposited and the filter is "pre-coated." During the "filter cycle," contaminated coolant is passed through the filter in the same direction as the fluid flow during the pre-coat cycle. The expected lifetime of this resin is 14 to 21 days, under normal operating conditions; however, resin exhaustion is extremely rapid in the event of in-leakage of raw water from the condenser.

The filter is used until the pressure drop across it, or the conductivity in the effluent, shows it has been exhausted. It then goes through the "backwash cycle."

APPLICATIONS

Ion-exchange and filtration processes are used in various systems in a nuclear power plant. Applications to primary coolant purification systems for a PWR and a BWR are presented in the next section of this module. Radwaste disposal is discussed in a later module. Make-up water, which uses these techniques for raw-water polishing before it enters the reactor systems, was discussed previously. The spent-fuel system uses demineralization to remove fission products from fuel elements that may be leaking because of cracks in the fuel cladding.

REACTOR PRIMARY WATER PURIFICATION SYSTEM

Purification of water in the primary system of a PWR or BWR is accomplished, primarily, by demineralizers and filters (discussed previously).

PURIFICATION HALF-LIFE

Rate of removal of impurity from the primary system can be described in terms of purification half-life, the time required to reduce the concentration of any impurity in the coolant to one-half its initial concentration. (This value is similar to the half-life of a radionuclide.) The numerical value of a half-life, $T_{\frac{1}{2}}$, is derived as follows:

$$T_{\frac{1}{2}} = 0.693 \frac{\text{(reactor coolant volume)}}{\text{[flow (gpm) in clean-up system]}}$$

Eq. 13-4-5

This purification half-life, which is useful during periods of upset water quality when it is desirable to know how fast the upset condition can be returned to normal, is more readily determined from a graph of Equation 13-4-5 (Figure 13-4-4) for various values of flow rates and reactor coolant volumes. For example, assume a reactor coolant volume of 100,000 gallons and a purification system that takes 80 gallons per minute of this coolant and purifies it with 100% removal each pass through the purification demineralizers. From the graph, about 14 hours is the indicated half-life.

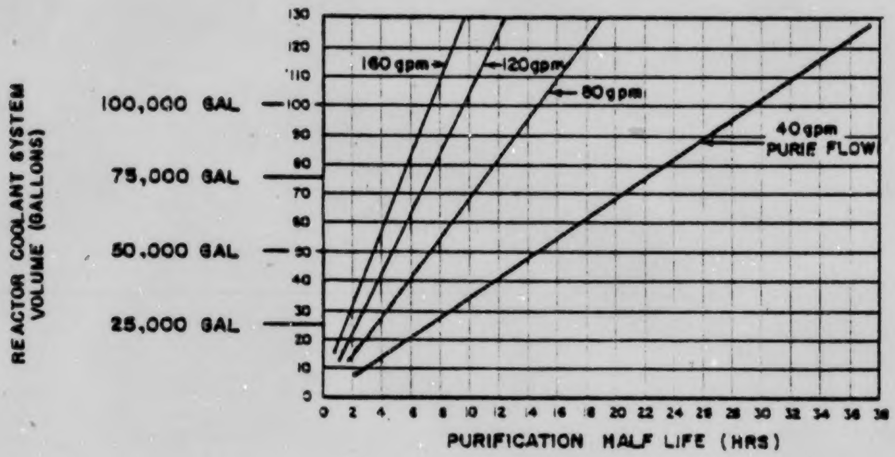


Figure 13-4-4. Relationship of reactor coolant volume to purification half-life.

Effectiveness of purification system in removing contaminants from coolant is described in terms of the decontamination factor (DF):

$$DF = \frac{\text{activity present at start of purification}}{\text{activity present at end of purification}}.$$

Eq. 13-4-6

DF is the ratio of radioactivity per milliliter of coolant measured at the beginning and end of the purification cycle. This same concept also can be applied to determine the efficiency of removal of contaminants by a single piece of purification equipment, such as a filter or demineralizer:

$$DF = \frac{\text{activity at inlet to equipment}}{\text{activity at outlet from equipment}}. \qquad \text{Eq. 13-4-7}$$

In addition to the required control of corrosion and fission products, some way must also be devised to regulate reaction products formed by radiolysis of water, and air in-leakage.

RADIOLYSIS OF WATER

Exposure of coolant to reactor radiation results in dissociation of water into reactive species (e.g., atoms of H, OH, and so on). These primary reaction products recombine to give hydrogen or oxygen gas at reactor temperatures:

$$2H_2O \rightleftharpoons 2H_2 + O_2. \qquad \text{Eq. 13-4-8}$$

Water decomposition by gamma radiation is favored during power operation, and water formation is favored during shutdown.

In-leakage of nitrogen and oxygen from the atmosphere can produce nitric acid in the coolant:

$$2H_2O + 2N_2 + 5O_2 \rightarrow 4HNO_3. \qquad \text{Eq. 13-4-9}$$

Quantity of nitric acid formed is directly proportional to reactor power. Nitric acid is undesirable because it attacks and dissolves the film that inhibits corrosion of steel piping and reaction vessels. In a PWR, production of this acid can be reduced by addition of hydrogen gas, which is dissolved in the coolant:

$$2HNO_3 + 5H_2 \rightarrow N_2 + 6H_2O. \qquad \text{Eq. 13-4-10}$$

Notice that addition of hydrogen gas in the PWR also causes recombination with the oxygen produced by radiolysis of water (i.e., it causes Equation 13-4-8 to be reversed). In a BWR, the gases formed by radiolysis are generally removed by the air ejector in the condenser.

Typical water quality, which the purification system tries to maintain, is shown in Table 13-4-3. Detailed rea-

TABLE 13-4-3

MAXIMUM CONCENTRATION OF IMPURITIES IN LIGHT-WATER REACTOR PRIMARY SYSTEMS

Impurity	PWR Primary Coolant	BWR Feedwater
Total solids	1.0 ppm	< 30 ppb*
Dissolved oxygen	none	200 ppb
Lithium as ^7Li	0.5 - 2.0 ppm	—
Hydrogen (cc/kg H_2O)	15 - 40	0.4
Chlorides	0.1 ppm	0.1 ppm
Fluorides	0.1 ppm	0.1 ppm
Boric acid	13,000 ppm	30 ppm

* Fe, Cu, Ni, Cr, both soluble and insoluble forms.

sons for each of these values were discussed in a previous module.

PURIFICATION SYSTEM - BWR

Water is removed from a BWR primary system through a recirculation pump suction line (Figure 13-4-5). During normal operation, water is continuously removed at reactor temperature and pressure and then pumped through regenerative and nonregenerative heat exchangers. The heat exchangers cool the reactor water to temperatures compatible with operational limits of ion-exchange resins in the filter de-

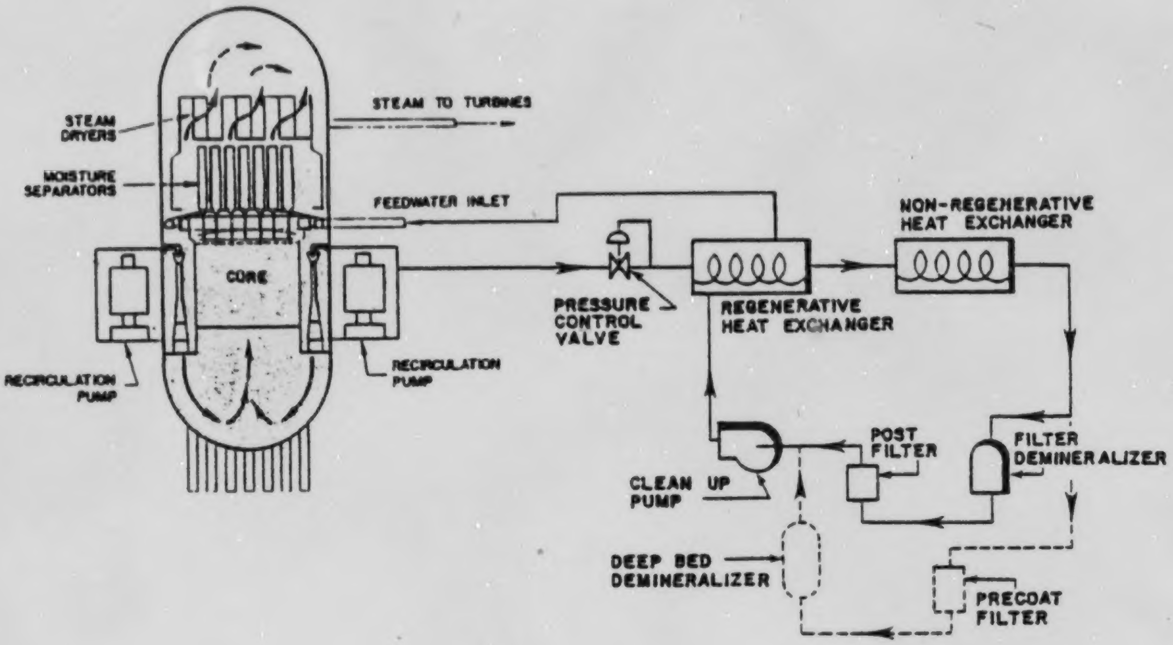


Figure 13-4-5. Typical BWR reactor cleanup system.

mineralizer or deep-bed demineralizer. Impurities are removed, and the water flows back through the shell side of the regenerative heat exchanger (where it absorbs heat). The water then returns to the feedwater to become boiler feed. During startup (and other times of increasing water volume), excess water is normally removed from the reactor by blowdown through the purification (cleanup) system to the main condenser or waste tanks.

Operation of the reactor water cleanup system is controlled from the main control room. Filter resin backwashing and pre-coating operations are controlled from a local panel. The cleanup system is isolated from the reactor automatically by closure of motor-operated isolation valves on any of the following signals:

High temperature after nonregenerative heat exchanger.
Low reactor water level.
High ambient temperature in cleanup system equipment area.
High flow rate differential between system inlet and outlet.
High differential temperature across primary containment ventilation system.

Removal of hydrogen, oxygen and air (by air ejectors) is discussed in a later module.

PURIFICATION SYSTEM - PWR

The purification system of a PWR is more complex than that of a BWR because it also supplies chemicals to the primary system which assist in control of the reactivity of the core. In a PWR, as shown in Figure 13-4-6, reactor

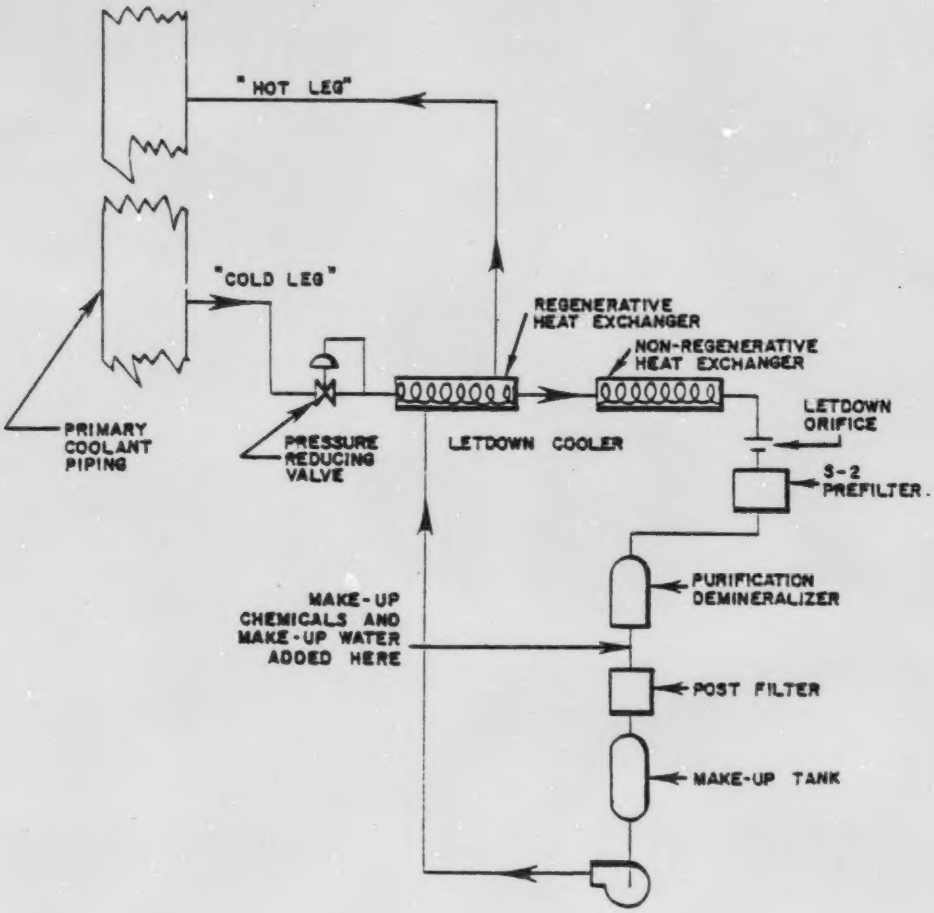

"HOT LEG"
"COLD LEG"
REGENERATIVE HEAT EXCHANGER
NON-REGENERATIVE HEAT EXCHANGER
LETDOWN ORIFICE
PRIMARY COOLANT PIPING
PRESSURE REDUCING VALVE
LETDOWN COOLER
S-2 PREFILTER.
PURIFICATION DEMINERALIZER
MAKE-UP CHEMICALS AND MAKE-UP WATER ADDED HERE
POST FILTER
MAKE-UP TANK

Figure 13-4-6. PWR chemical purification system.

water is removed through heat exchangers, which cool the fluid, and through a letdown orifice, which reduces its pressure to slightly above atmospheric. This adjustment is necessary to protect the purification demineralizers - operating temperatures limited to a maximum of 140°F (60°C).

Chemicals and make-up water are added before coolant is reheated and returned to the primary piping system.

Several types of chemicals are added between the purification demineralizer and the post filter: lithium hydroxide is added to control pH primarily [i.e., to keep reactor coolant neutral - or slightly basic - at normal reactor operating temperatures (Figure 13-4-7)]. The ba-

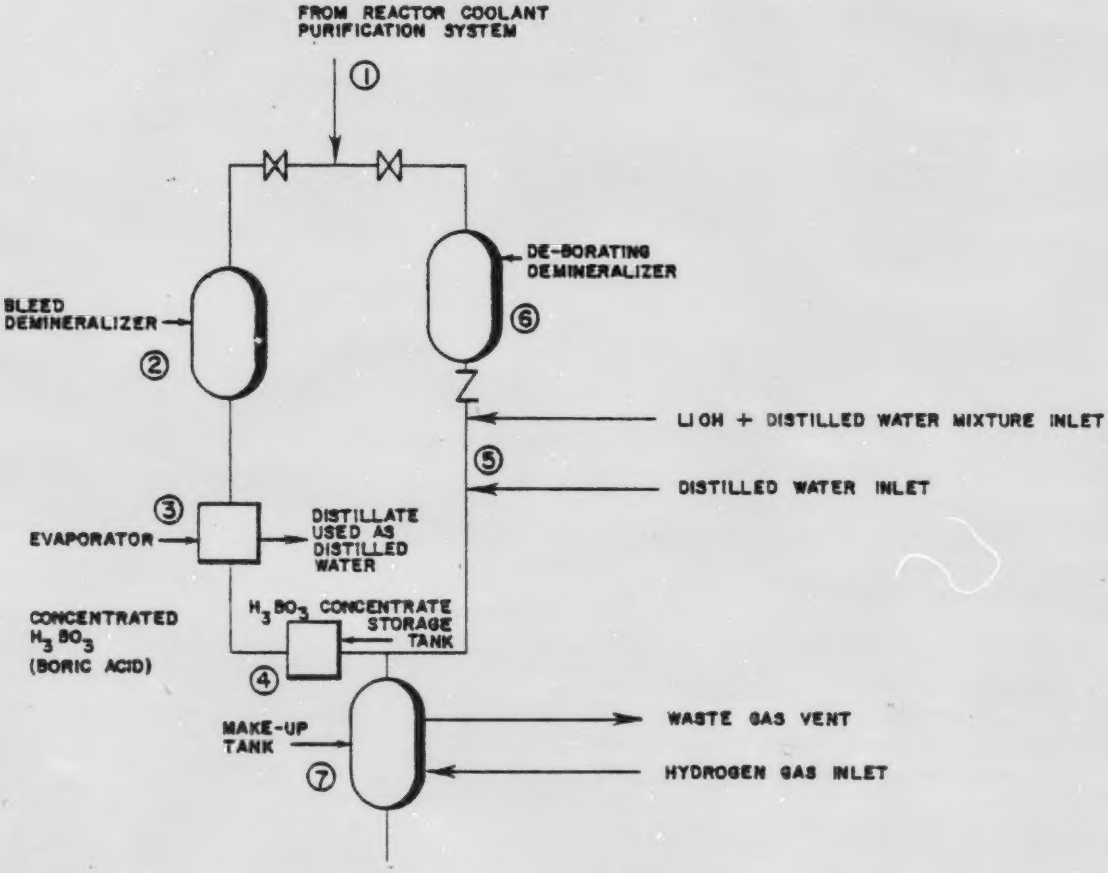

FROM REACTOR COOLANT PURIFICATION SYSTEM
①
DE-BORATING DEMINERALIZER
⑥
BLEED DEMINERALIZER
②
LiOH + DISTILLED WATER MIXTURE INLET
⑤
DISTILLED WATER INLET
③
EVAPORATOR
DISTILLATE USED AS DISTILLED WATER
H_3BO_3 CONCENTRATE STORAGE TANK
CONCENTRATED H_3BO_3 (BORIC ACID)
④
MAKE-UP TANK
⑦
WASTE GAS VENT
HYDROGEN GAS INLET

Figure 13-4-7. Chemical and volume control system.

sicity of lithium hydroxide is adjusted (at operating temperatures) to offset the acidity of boric acid in the coolant.

Lithium hydroxide also helps reduce the concentration of insoluble metal oxides suspended in the circulating system. Also, it helps agglomerate colloidal crud particles by increasing coolant conductivity, which helps particles to neutralize their surface charges.

CHEMICAL AND VOLUME CONTROL SYSTEM - PWR

A chemical and volume control system regulates hydrogen, lithium hydroxide and boric acid concentrations in reactor coolant. This system also corrects for increases in water volume (during startup, shutdown and normal operation).

Boric Acid Feed and Bleed System

Boric acid is added to reactor coolant to control the concentration of boric acid (Figure 13-4-7). Boric acid is removed from primary coolant, through the letdown system and the purification demineralizer, to point 1. At the same time, demineralized water is added back into the reactor coolant at point 5. Meanwhile, the boric acid passes unchanged through the "bleed" demineralizer, point 2, which was previously saturated with borate ions. The evaporator, point 3, concentrates the boric acid, which is pumped into the concentrated boric-acid tank, point 4, for storage. To add concentrated boric acid to the coolant, 50,000 ppm is pumped from the storage tank, point 4, through the makeup tank into the reactor coolant. At the same time, dilute boric acid is removed from the coolant, at point 6, to keep coolant volume relatively constant.

The "bleed demineralizer" is part of the control system for the lithium-7 hydroxide concentration in the reactor coolant. Concentrated lithium hydroxide is added at point 5 to increase coolant lithium; at the same time, dilute lithium solution is removed by the bleed demineralizer at point 2. To dilute lithium concentration in the coolant, the process is reversed.

The "de-borating demineralizer," point 6, removes boric acid from the coolant when its concentration has been reduced to around 30 ppm by the feed and bleed system. The anion resin is in the hydroxide form with a volume of several tens of cubic feet. Borate ions in the circulating solution replace hydroxide ions on the resin and become bound to the resin. These resins are normally regenerated to recover boric acid.

Control of the gas phase in the primary system is accomplished through the make-up tank, point 7. Waste gas is automatically vented to the gaseous radwaste system from the space over the make-up tank solution. Hydrogen gas is also automatically added to the proper partial pressure above the water to maintain the desired concentration of dissolved hydrogen gas in reactor coolant.

Evaporator System - Operating Variables

The evaporator (in the chemical and volume control system) produces two effluent streams: 1) a concentrated solution containing 50,000 ppm of boric acid and 2) a dilute solution containing around 57 ppm of boric acid.

The most common evaporator used to recover boric acid is a single-effect type (Figure 13-4-8). Evaporation is a purely mechanical process, removing dissolved and suspended solids from the feed by vaporizing water with heat.

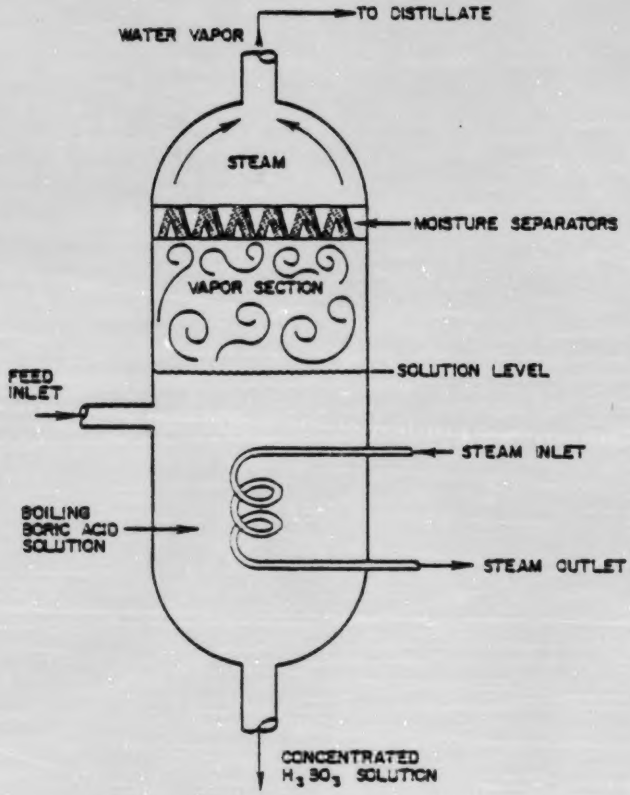


Figure 13-4-8. Single-effect, horizontal-tube evaporator.

The process is carried out in a pressure vessel through which steam-heating coils pass. This steam heats the feed to boiling and drives off water in the form of steam, called distillate. When cooled, distillate is relatively pure water. The concentrated solution, which collects in the bottom of the evaporator, is called "bottoms."

Distillate purity is determined by operating conditions and evaporator design. Good design prevents tiny water droplets (which contain dissolved impurities) from "boiling over"

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with the distillate. Boilover (or carryover) is prevented by keeping the evaporation rate constant, which is controlled by steam pressure. If the evaporator liquid level is maintained below boilover level, little carryover occurs. For this reason, the feed may be controlled automatically by an automatic flow-control device. A demister, included in all evaporators, traps liquid droplets that manage to boil over.

Evaporator use is not confined to PWR chemical and volume control systems. They are used extensively in waste treatment, which will be discussed in a later module. Also, they are used as the first step in raw-water treatment when large quantities of dissolved solids are present. Evaporation removes a large portion of dissolved solids, while demineralizers remove most of the rest (in a final polishing phase, following evaporation). The net result is reactor make-up water.

EXERCISES

1. How does a laboratory technician normally separate insoluble corrosion products in reactor cooling water from soluble corrosion products? Explain.
2. During regeneration of a mixed-bed ion exchanger, dilute acid flow rate is roughly 20% higher than that of the dilute caustic (caused by operator error). What is probable (qualitative) effect on output water quality? What can be done to correct the situation?
3. If a PWR does NOT have letdown systems (for reducing

pressure and temperature), describe the effect on the following:

Capacity (eq/l) of ion exchanger.
Reactor coolant system water quality.

4. Why is NaOH not used (in a PWR, to adjust pH) instead of LiOH, which costs more per pound?
5. What is the ion-exchange capacity of a mixed-bed demineralizer (eq/l) that contains 2 volumes of cation to 1 volume of resin?
6. If purification rate (cleanup rate) of a BWR is 80 gpm (at 120°F), how long will it take (in hours) to reduce 64 ppb of Co-60 to 1 ppb after a "crud burst?" (Assume BWR coolant volume is 120,000 gallons and 100% removal of Co-60 per pass.)
7. Determine decontamination factor for purification system described in Exercise 6 if 1 ppb is the final concentration of soluble Co-60 in the reactor coolant.

MATERIALS

ION EXCHANGERS

1 set pH indicator strips (nonbleeding) for use pH 0-14, in increments of one pH unit.
4 100 milliliter beakers.
1 liter 0.1M H_2SO_4 (17.8 M or 95%); dilute to 1 liter with distilled water.

1 liter 0.1M NaOH solution (dissolve 4.2 grams of solid in water; dilute to 1 liter).

2 containers, approximately 1.5 liters each.

1 pipette, 10 ml, graduated in 0.1-ml divisions.

1 laboratory balance, accurate to 0.05 grams.

1 demonstration kit, 6 amberlite ion-exchange resin tubes, model No. 3334 Mallinckrodt Chemical Works, St. Louis, Mo. (or equivalent).

2 ringstands and 2 adjustable clamps to hold resin column.

1 separatory funnel, 100 ml.

1 piece of tubing to connect funnel to resin container.

DEMINERALIZERS

1 demonstration kit, 6 amberlite ion-exchange resin tubes, model No. 3334, Mallinckrodt Chemical Works, St. Louis, Mo. (or equivalent).

1 separatory funnel, 500 ml.

1 piece of hose to connect separatory funnel to demineralizer container.

20 beakers, 25 ml, for collection of conductivity samples.

1 container, approximately 1 liter.

250 ml salt solution, 0.07M (4044 ppm) NaCl; add 2.03 grams of salt to 0.5 liter of distilled water (or use sea water).

1 laboratory balance, accurate to 0.05 grams.

1 100-ml graduated cylinder.

1 ringstand and 2 adjustable clamps to hold funnel and demineralizer.

1 conductivity meter (0.05 to 1000 μmhos/cm) and conductivity cell (cell constant should be 0.1).

FILTRATION

1 filter housing (3/4" P.T. fittings).
1 cartridge filter, inlet/outlet (3/4" P.T.).
1 garden hose (0.5 - 1" I.D.).
1 collector (a clean garbage can or plastic bucket).
2 metal adapters: garden hose to 3/4" pipe threads.
Several grams of colloidal iron oxide (Fe_3O_4) I - 119 (Fisher Chemical Co. Black).
1 laboratory balance, sensitive to 0.01 gram.

PROCEDURES

ION EXCHANGERS

1. Wash and prepare ion-exchange resins as recommended by manufacturer. CAUTION: KEEP WATER LEVEL ABOVE TOP OF RESIN BED AT ALL TIMES.
2. Close stopcocks on separatory funnels; connect each resin container to a separatory funnel with tubing; fill tubing space with water and remove air bubbles.
3. Pour 30 ml of 0.1M H_2SO_4 and 30 ml of 0.1M NaOH into

separate beakers; pour acid into funnel connected to anion resin; pour base into funnel connected to cation resin.

4. Measure approximate pH of solutions (use pH papers); record pH on Data Table 13-4-1.
5. Add 30 ml of 0.1M H_2SO_4 to anion exchanger at rate of about 5 ml/min; collect effluent in 100-ml beaker.
6. Measure pH of effluent; record on Data Table 13-4-1.
7. Add 30 ml of 0.1M NaOH to exchanger at rate of about 5 ml/min; collect effluent in 100-ml beaker.
8. Measure pH of effluent; record on Data Table 13-4-1.
9. Discuss results.

DEMINERALIZERS

1. Wash and prepare demineralizer resins as recommended by manufacturer. CAUTION: KEEP WATER LEVEL ABOVE TOP OF RESIN BED AT ALL TIMES.
2. Connect separatory funnel to demineralizer with tubing; fill the tubing space with water and remove air bubbles; close stopcock on empty separatory funnel.
3. Fill separatory funnel with about 250 ml of salt solution.
4. Select one (of 20) beaker; place it under demineralizer.
5. Open stopcock; adjust flow to about 6 ml/min; fill beaker about two-thirds full.
6. Measure volume of solution to nearest 0.1 ml. (It should be 15-17 ml.)

7. Measure conductivity of solution as follows:
    a. Immerse conductivity cell in solution. Electrodes should be immersed at least 1 cm.
    b. Connect cell to conductivity meter.
    c. Set multiplier switch at an intermediate position; rotate main control dial full length of scale. If null-current balance point cannot be attained on this scale, change scales and repeat until balance is attained.
    d. Multiply main scale reading by this scale factor to record conductance of solution in micromhos; record this value on Data Table 13-4-2.
8. Continue to collect samples and measure their conductivities, as in steps 5, 6 and 7, until 16 samples are collected (or until a null balance is no longer possible with the cell); record all values on Data Table 13-4-2.
9. On linear graph paper, plot collected volume (horizontal axis) versus conductivity (vertical axis); connect points with a smooth curve line; draw tangent line to horizontal and to rising part of curve. The intersection of these two lines marks breakthrough point of demineralizer. Alternately, use conductivity of 0.5 micromhos/cm as rough breakthrough point of demineralizer.
10. Discuss results.

FILTRATION

1. Add 0.14 gram of black iron oxide to transparent fil-

ter housing.

2. Fill with water, and shake (to suspend black particles).
3. Connect adapters to each side of filter housing; connect garden hose to a fresh-water tap, and to the inlet side of the filter; connect another piece of hose to outlet side, and dip into collector.
4. Flush water through the filter; note clarity of effluent.
5. Discuss results.

DATA TABLE

DATA TABLE 13-4-1

		Approx. pH
1.	pH of 0.5M H_2SO_4 solution	________
	pH of 0.5M NaOH solution	________
2.	pH of effluent cation resin	________
	pH of effluent anion resin	________

3. Write chemical equations to show how:
   a. Cation resin removes sodium ion:

   $$CR{-}{-}{-}{-}H + Na^+ + OH^- \longrightarrow \underline{\qquad\qquad} + \underline{\qquad\qquad}$$

   b. Anion resin removes sulfate ion:

   $$AR{-}{-}{-}{-}OH + 2H^+ + SO_4{-2} \longrightarrow \underline{\qquad\qquad} + \underline{\qquad\qquad}$$

4. Explain (use step 3) changes in pH observed between steps 1 and 2 (above).

DATA TABLE 13-4-2

Beaker Number	Volume Collected	Conductivity μmhos/cm
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		
11		
12		
13		
14		
15		
16		
17		

Breakthrough point occurs at:

__________ ml of solution or __________ μmhos/cm.

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TEST

1. Briefly explain theory of each of the following:
   - Ion-exchange softening of water.
   - Evaporation.
   - Demineralization.
   - Pre-coat filtration.

2. List typical values for the following ion-exchange softening system parameters:
   - Maximum operating temperature.
   - Exchange capacity.
   - Moisture content.

3. List typical values for the following demineralizer system parameters:

Maximum operating temperature.

Cation and anion exchange capacity.

Flow rates through the exchangers.

Moisture content.

4. Sketch PWR and BWR coolant water treatment systems; briefly explain operation of each:

5. Sketch and briefly explain operation of an evaporation system:

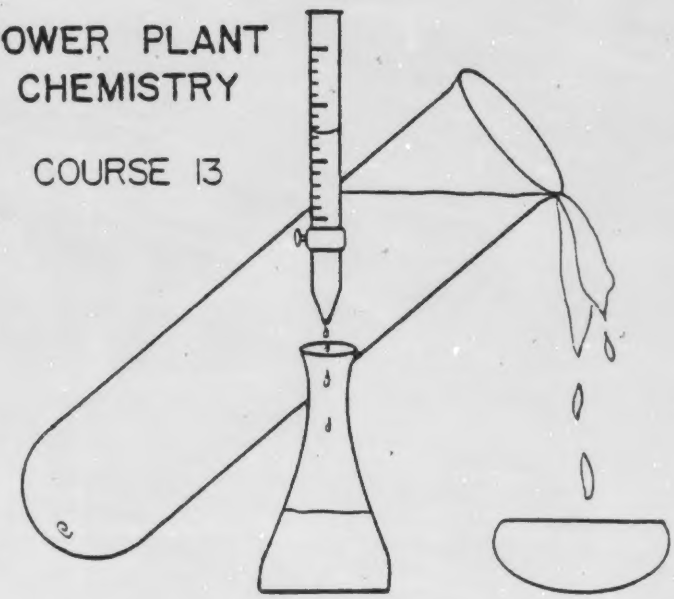
NUCLEAR TECHNOLOGY

MODULE 13-5 WATER PROPERTIES SENSING. -

ROBERT B. NEEL

POWER PLANT CHEMISTRY

COURSE 13



TERC-SW

TECHNICAL EDUCATION RESEARCH CENTER — SOUTHWEST
4201 LAKE SHORE DRIVE WACO, TEXAS

COURSE MODULES

COURSE 13 POWER PLANT CHEMISTRY

MODULE 13-1	Water Quality Control
MODULE 13-2	Raw-Water Treatment
MODULE 13-3	Sources of Impurities in Reactor Water Systems
MODULE 13-4	Water Treatment - Polishing by Ion Exchange, Evaporation and Demineralization
⇨ MODULE 13-5	Water Properties Sensing
MODULE 13-6	Water Analysis for Nuclear Power Plants
MODULE 13-7	Radioactive Waste Handling - Liquid and Gaseous

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INTRODUCTION

To ensure that reactor coolant water quality remains high at all times, it must be periodically sampled and analyzed.

This module describes several types of instrumentation used to monitor water quality. It emphasises instruments that continuously and automatically monitor in systems such as PWR and BWR primary and condensate feedwater.

MODULE PREREQUISITES

The student should have completed all previous modules in this Course.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Define and discuss principles of operation of the following (as used in power plant systems):
    - pH sensors.
    - Conductivity sensors.
    - Dissolved oxygen (DO) sensors.
    - Halide ion sensors.

Turbidimeters.

2. State why halide-detection is used in a power plant water system.
3. Briefly describe how a dissolved oxygen meter normally is employed in a reactor water system.
4. Set up a pH meter detector system to monitor a flowing water stream, (simulating water system in power plant).
5. Set up a DO meter air-leak detector system to monitor a closed loop of flowing water.

WATER PROPERTIES SENSORS

Water at 77°F (25°C) contains equal concentrations (10^{-7} moles/liter) of both hydrogen and hydroxyl ions, according to the following equilibrium reaction:

$$H_2O \rightleftarrows H^+ + OH^-.$$

Equation 13-5-1
(Equation = Eq.)

Hydrogen and hydroxyl ion concentrations are the same because water molecules dissociate into equal numbers of each kind of ion. The pH of a solution is defined as "the negative logarithm (to the base 10) of a hydrogen ion concentration in moles/liter;" therefore, the pH of a neutral solution of water is given as $pH = -\log (10^{-7}) = 7$; it is said to have a pH of 7.

A pH sensor is a transducer in which voltage output varies in proportion to pH (of solution measured), referenced to a voltage from a standard electrode:

$$\Delta E = \text{constant (pH)}. \qquad \text{Eq. 13-5-2}$$

The Δ refers to difference in potential (voltage) between two electrodes used in pH measurements (Figure 13-5-1). Both electrodes are immersed together into the solution to be measured. One electrode is used as a point-of-reference voltage; its potential stays constant throughout the measurement period.

Because the electrode is made of a paste of mercury chloride (calomel) and a saturated solution of potassium chloride, it is frequently referred to as a saturated calomel

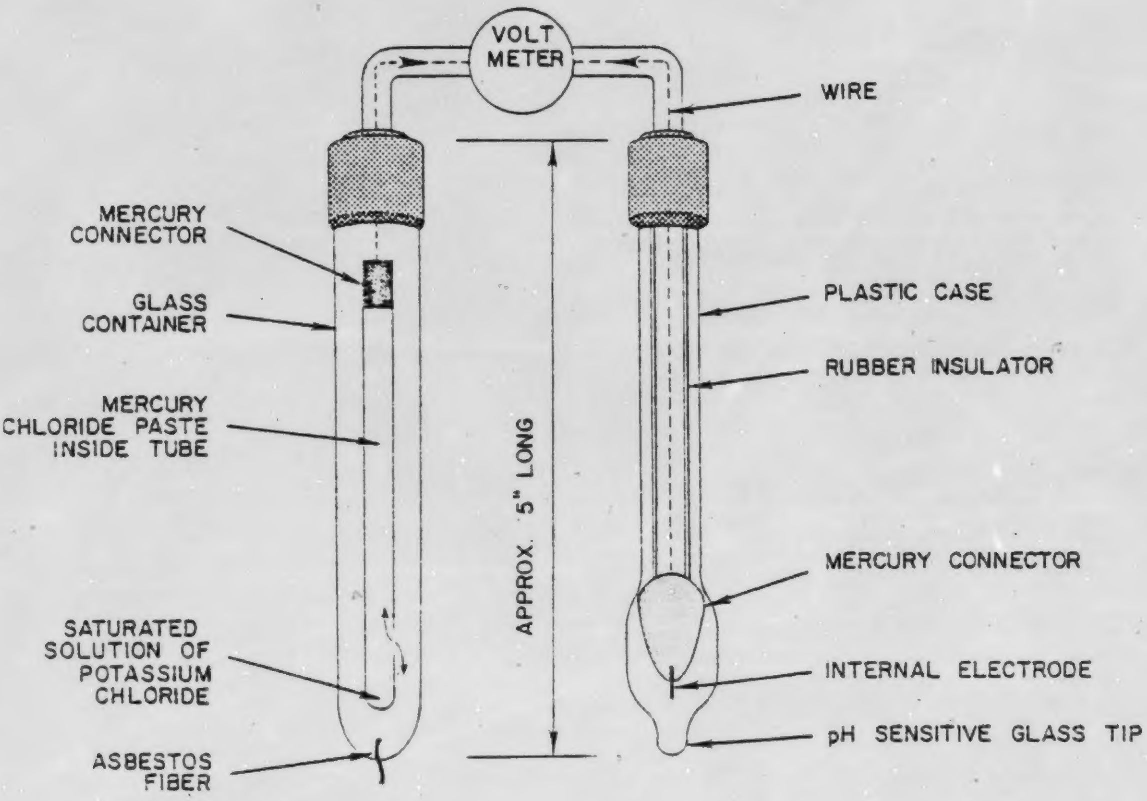

Figure 13-5-1. Electrode structure of a pH-monitoring system.

electrode (SCE). The other electrode, which is made of glass, contains a constant concentration of about 0.1 M hydrochloric acid. An electrical field is set up between the hydrogen ions inside and outside the glass. The size of the electrical field is proportional to the solution's pH value:

$$\Delta E = (E_{glass} - E_{ref}) = \text{constant (pH)}. \qquad \text{Eq. 13-5-3}$$

Voltage output of the glass electrode (relative to the reference electrode) changes in the same manner as the pH varies. A change of ± 1 pH unit might typically cause a change in output of about ± 59 millivolts. These differences in voltage are measured with a very sensitive, high-impedance voltmeter, scaled to read directly in pH units; the total assembly is called a "pH meter."

Although the two electrodes are shown (Figure 13-5-1) as separate units, sometimes both tubes are combined into a single assembly. This single assembly may be protected by a strong casing of metal or thick plastic to provide structural strength for industrial applications. Also, instead of using an asbestos fiber as an electrical connector to the solution, a porous ceramic plug may be substituted. The saturated solution of potassium chloride also may be solidified with a viscous gelatin to prevent rapid diffusion of ions into (or out of) the reference cell.

Temperature of the solution being measured has a significant effect on pH measurement. Two solutions, with the same hydrogen ion concentration, but of two different temperatures, give different readings on a pH meter; the solution with the higher temperature provides a larger electronic signal voltage, and the voltmeter interprets this as a larger pH value.

Most manufacturers incorporate manual compensation for this error if solution temperature is not predictable.

Because the upper useful temperature limit of pH electrodes is, at most, 212°F (100°C), the temperature of reactor coolant must be reduced before an accurate pH measurement is attempted.

The electronic signal output of a pH meter electrode follows Equation 13-5-3 quite closely. (For more accurate values, a special standardization procedure is usually followed.) During normal reactor operations, an operator is interested primarily in a constant value of pH, rather than a highely accurate one. Changes in pH are interpreted as upset conditions requiring corrective action.

PRINCIPLES OF OPERATION OF A CONDUCTIVITY SENSOR

Conductivity sensor operation is based on the fact that salts, which form ions in solution, conduct current if a voltage is applied across the solution. In an ideal situation, the applied voltage is between two parallel plates, of a given area, immersed in the solution of interest at a given separation. Positive ions drift toward the negative plate, while negative ones drift toward the positive plate (Figure 13-5-2).

Negative ions give up electrons at the anode; they then flow through the wire because they are attracted to the positive pole of the battery. imultaneously, other electrons leave the negative pole of the battery and neutralize positive ions that have drifted to the cathode plate. These continuous movements of electrons through the wire, and simultaneous movements of ions through the solution, constitute a current that can be measured by an ammeter in the

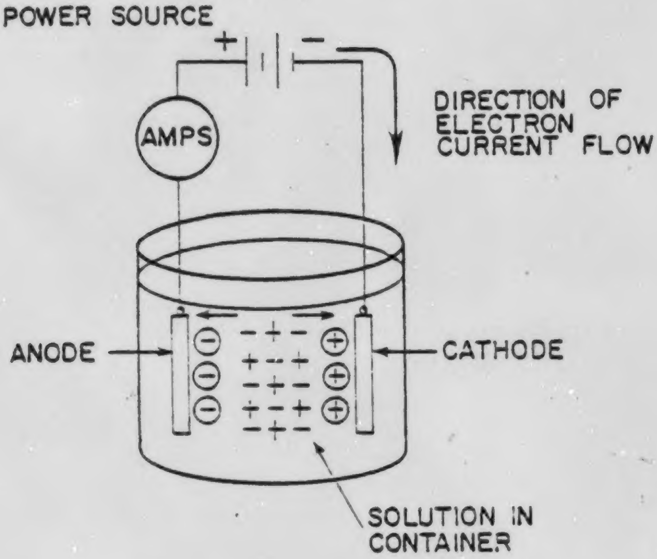

Figure 13-5-2. Current in a solution containing ions.

circuit. The greater the current, the less the resistance of the solution to the flow of current (i.e., the higher the conductivity).

Resistance in a solution is defined as follows:

$$\text{resistance (ohms)} = \frac{1}{\text{conductance (mho)}}.$$

Eq. 13-5-4.

EXAMPLE

A conductance of one micromho means that the solution in a cell offers the following resistance to the flow of current through the cell:

$$\text{Resistance} = \frac{1}{1.0 \text{ micromho}} = \frac{1}{10^{-6} \text{ mhos}}$$

$$= 10^{6} \text{ ohms} = 1 \text{ megohm.}$$

If the parallel plates (Figure 13-5-2) are each 1 cm^2 (area), and 1 cm apart, "specific conductance" of the contained solution is 1 micromho/cm of solution length. Ultrapure water has a conductivity of about 0.054 μmhos/cm at 25°C (77°F). (Conductivity also depends upon temperature.) The "conductivity" of a solution is the sum of the conductivities of each of its individual ions.

Because ions in solution move at different speeds toward an anode or cathode plate (Figure 13-5-2), the same concentration of different ions gives different values of specific conductance. Table 13-5-1 lists the concentrations of selected ions (in ppm) necessary to produce a specific conductance of 1.0 μmho/cm when no dissolved gases are present. Only minute changes in the concentrations of hydrogen (or hydroxyl) ions are necessary to produce the desired conductivity compared to that of the other ions.

TABLE 13-5-1

APPROXIMATE CONCENTRATIONS OF IONS (ppm) REQUIRED TO PRODUCE A SPECIFIC CONDUCTANCE OF 1.0 µmhos/cm IN DILUTE WATER SOLUTION (IF NO DISSOLVED GASES ARE PRESENT) AT 25°C (77°F)

Ion	ppm
H^+	0.003 ∿ (pH 5.5)
OH^-	0.089 ∿ (pH 8.7)
Ca^{++}	0.33
Na^+	0.45
$\overline{CI}^{=}$	38.00
$H_2BO_3^-$	800.00
NH_4^+	0.24
HCO_3^-	0.88
Cl^-	0.47
PO_4^{-3}	0.45

Commerical conductivity sensors come in different forms (Figure 13-3-3); however, each type produces an output current proportional to the number (and type) of ions dissolved in the solution being measured. Only one signal lead leaves the dip-cell or flow-cell shown on the bottom of the figure; the circuit is completed through the metal casing of the conductivity cell and the pipe (or tank) into which it is fitted. Dip-cells and flow-cells normally can be used up to 650°F (343°C) and in pressures up to 2000 psig if special cell casings are employed. Such sensors might be used to monitor the relative conductivity of the primary reactor coolants on a continuous basis.

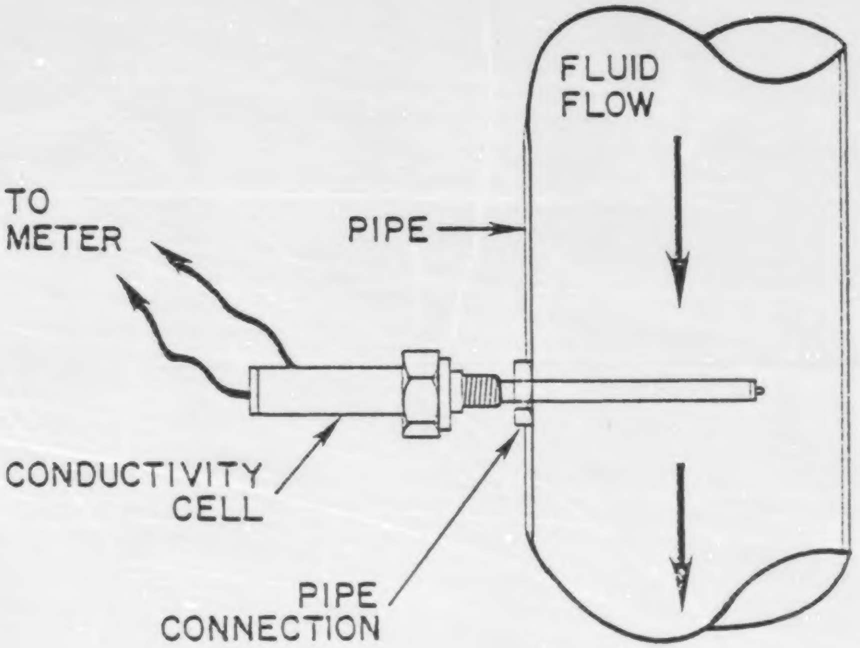

Figure 13-5-3. Typical industrial-type conductivity sensor (cells).

Cell constant is that number, which - when multiplied by actual reading of a conductivity meter (in micro-mhos) - gives specific conductance (in micromhos/cm).

Specific conductance (micromhos/cm) = reading (micromhos) x cell constant (in 1/cm). Eq. 13-5-5.

The other conductivity sensor (at the top of Figure 13-5-3) is submersible. Current flow between the pin-like electrodes (1 and 4) is proportional to the conductance of the solution. Electrodes 2 and 3 are voltage-control electrodes (their function is discussed later). The maximum useful temperature for this sensor is normally 122°F (50°C). (Reactor cooling water is frequently cooled to 25°C (77°F) to make laboratory measurements. Its response time to changes in conductivity is relatively slow, up to 2 minutes to attain 98% of its appropriate output voltage at a new conductivity level, depending upon how drastic the change is.)

DISSOLVED OXYGEN SENSOR OPERATING PRINCIPLES

Because of its tendency to promote corrosion, the oxygen concentration dissolved in water must be maintained at very low levels, usually below 0.1 ppm. A dissolved oxygen (DO) sensor can be used to continuously monitor dissolved oxygen concentration. The most frequently employed sensors for dissolved oxygen - membrane-type probes - offer certain advantages:

Membrane prevents potentially interfering gaseous or particulate matter from reaching probe electrodes.

Reagents do not need to be added continuously to solution inside cell in which electrodes are immersed.

In a polarographic type of dissolved oxygen sensor (Figure 13-5-4), current flows to the gold cathode, where the oxygen is reduced (i.e. gains electrons), through the solution to the silver anode, where the silver is oxidized (i.e., it loses electrons), and back to the positive battery pole. Simultaneously, an equal number of charges move from the negative pole of the battery through the current meter and back again to the gold cathode to complete the circuit.

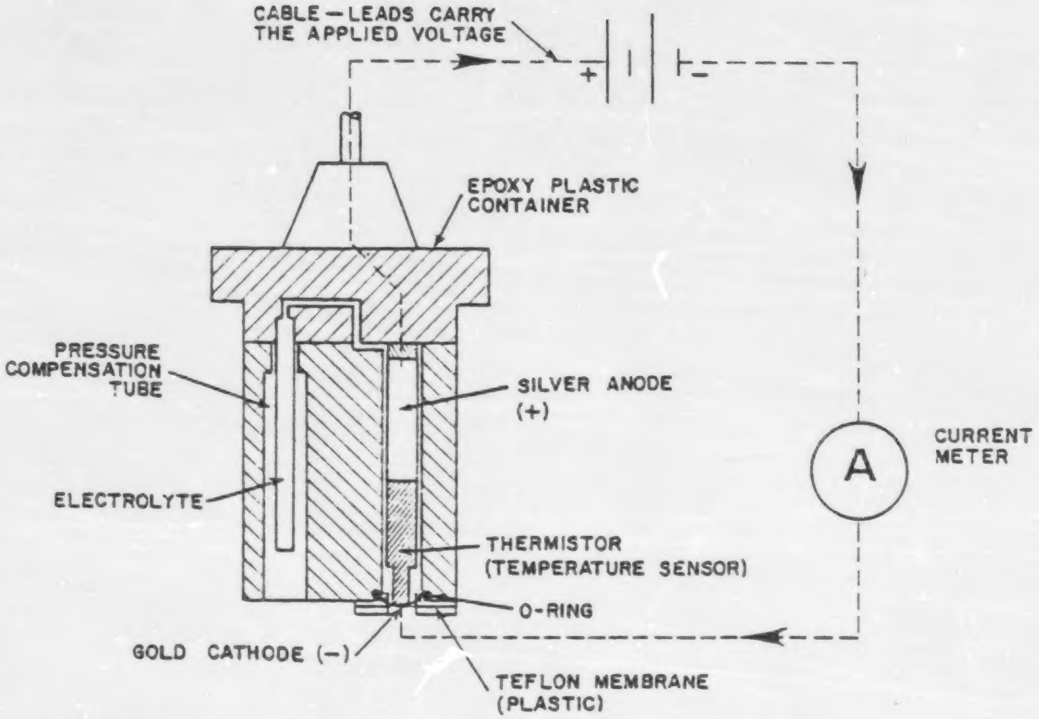
CABLE — LEADS CARRY THE APPLIED VOLTAGE
+
−
EPOXY PLASTIC CONTAINER
PRESSURE COMPENSATION TUBE
SILVER ANODE (+)
CURRENT METER
A
ELECTROLYTE
THERMISTOR (TEMPERATURE SENSOR)
O-RING
GOLD CATHODE (−)
TEFLON MEMBRANE (PLASTIC)

Figure 13-5-4. Galvanic type sensor for measuring dissolved oxygen.

This flow of current through the ammeter is proportional to the flow of oxygen through the membrane into the cell. The flow through the membrane is proportional to the concentration of dissolved oxygen. Thus, indicated meter current is proportional to DO content of solution being measured.

Chemical reactions occuring at the electrodes are analagous to those occuring in a conductivity cell:

Silver Anode: $4\,Ag^{\circ} + 4\,Cl^{-} \rightarrow 4\,AgCl + 4$ electrons.

Gold Anode: 4 electrons $+ O_2 + 2H_2O \rightarrow 4\,OH^{-}$.

Eq. 13-5-5

Oxygen, when it diffuses into the gold cathode, picks up four electrons; simultaneously, four different electrons are transferred by the silver dissolving from the anode. Other types of oxygen-membrane systems generate their own current-driving force internally, without the use of a battery. These galvanic sensors operate in a manner similar to the polarographic type discussed above.

Several special features of the on-line, continuous dissolved oxygen monitor deserve further mention. The monitor should be mounted in a simple flow cell, which provides for a turbulent flow (of the sample to be tested) past the probe membrane at a rate of over 100 milliliters/minute. This arrangement ensures that the layer of dissolved oxygen next to the membrane is not depleted, and it represents the oxygen content in the bulk of the solution. The sample temperature must be known for an accurate determination of dissolved oxygen concentration (in ppm) with a membrane electrode. (Table 13-5-2 shows that the solubility of dissolved oxygen decreases with increasing temperature of the solution.) The oxygen-diffusion rate through the membrane also changes with temperature; thus, a correction must be applied to obtain an accurate indication.

Normally, samples are not measured at temperatures above 113°F (45°C) and measurements made above 25°C must be corrected. This correction is usually accomplished by a temperature compensation network. For these reasons, a thermistor (temperature-sensitive resistor) frequently is included in the measuring container (Figure 13-5-4).

TABLE 13-5-2.

SOLUBILITY OF OXYGEN GAS IN "PURE" WATER AS A FUNCTION OF TEMPERATURE

Solution Temperature		Max. Amount (in cc) O_2/Kilogram H_2O
°F	°C	
32	0	10.2
50	10	7.9
77	25	5.8
104	40	4.5
176	80	2.0
212	100	0.0

The solubility of nitrogen is approximately twice that of oxygen at the same temperature.

HALIDE ION-SENSOR OPERATING PRINCIPLE

The most common use of halide ion sensors (in a nuclear power plant) is for monitoring chloride ions and two principle types of these sensors are used.

More commonly used for continuous monitoring in the 50 to 200 ppb range, is the mercuric thiocyanate color method. Principles of color analysis (spectrophotometer) are thoroughly discussed in Module 13-6, "Water Analysis for Nuclear Power Plants."

The other method, now under development, uses a special membrane electrode for chloride ion concentration measurement (from less than 10 ppb to several hundred ppb). The membrane electrode, which contains a mixture of silver chloride (and other chemicals), when used with a suitable reference electrode, develop an output voltage proportional to the concentration of chloride ions in solution.

TURBIDIMETER PRINCIPLES OPERATION

The turbidimeter is used to measure the quantity of insoluble suspended solids present in reactor waters. Filters remove most particles from reactor water greater than approximately 1 μmeter (4/100,000 in); however, the remaining circulating water contains very small particles (colloids). These tiny colloid particles can scatter light (as when sunlight passes through water containing a suspension of very fine dirt particles or when a beam of sunlight is "visible" in a smoky or dusty room). To measure the concentration of suspended particles in reactor water, a turbidimeter passes a strong beam of light through the sample. The amount of light scattered by the particles, measured by an appropriate light meter, is proportional to the concentration of solids (Figure 13-5-5).

Water, which contains suspended solids, enters continuously at point 1 and leaves, after anylysis, at point 2. An intense light, point 3, is focused with a lens into the flowing water stream. Scattered light, at right angles to the direction of motion of the flowing stream, is measured by a submerged photocell sensor, point 4; the signal is transmitted to the readout meter at the operator's console.

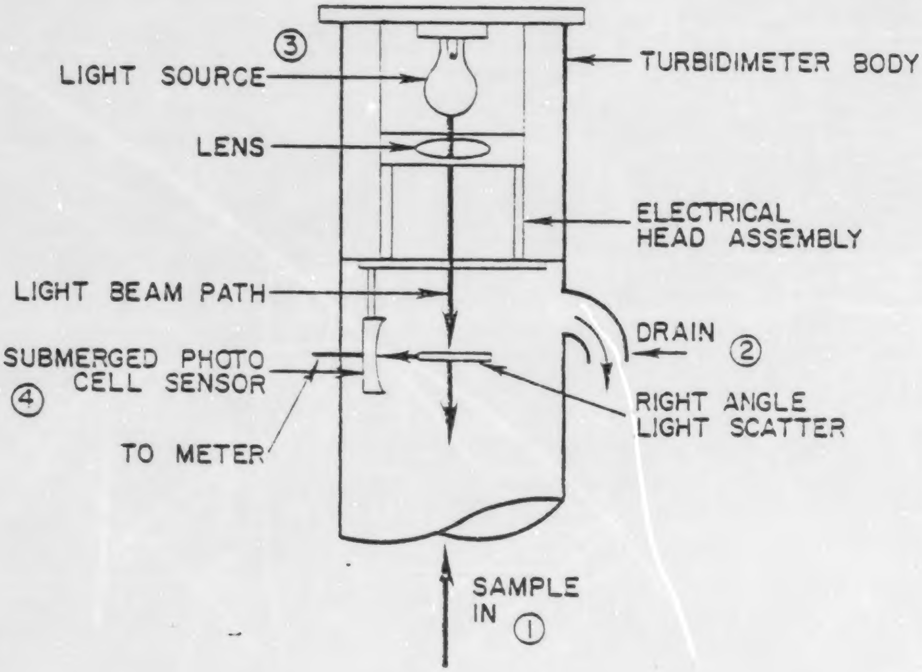

Figure 13-5-5. Commercial turbidimeter.

Because plastics are an important part of the structure of a turbidimeter, the operating temperature of the liquids sampled is usually restricted to a maximum of 113°F (45°C). The response of the instrument to changes in turbidity may be rather slow, requiring 15 seconds for a final, steady reading to be attained.

SAMPLE-POINT LOCATION FOR CONTINUOUS MONITORS

Sensors discussed in this module are used to continuously monitor important parameters in a BWR. Upper limits on the operating temperature of these sensors is about 122°F (50°C); the desirable temperature for measurements is about 77°F (25°C). Because the operating temperature of a BWR is about 545°F (285°C), water samples must be cooled and depressurized before being introduced into a sensor.

To reduce sample fluid temperatures, small heat exchangers ("coolers") may be employed on bypass lines (from a high-pressure/ high-temperature section to a sample point). Samples pass through these coolers, into the sensors, and then to liquid radwaste through waste drains (Figure 13-5-6).

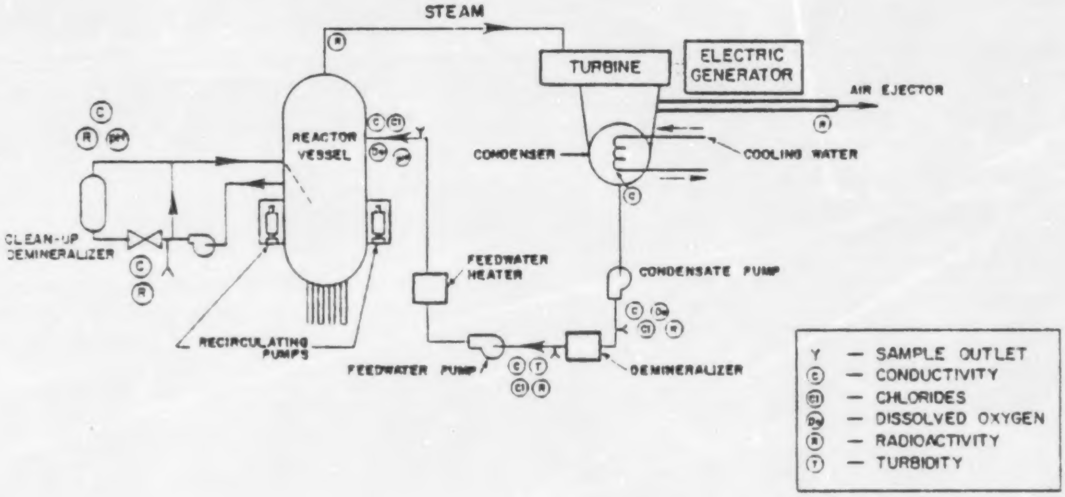

Figure 13-5-7. BWR sample points for continuous, on-line monitors.

hile taking a sample, a minimum sampling velocity of 2ft/sec is recommended (for liquids containing solids), to prevent settling of particles in the sample lines.

The radiation sensor, after the condensate demineralizer, is several orders of magnitude more sensitive to cation or anion buildup than the other chemical analyzers. It is used to signal depletion of ion-exchange resins at breakthrough.

The dissolved oxygen sensor reading after the high-pressure feedwater heater may be compared to the reading after the condensate pump to determine if any air in-leakage has occured between the condenser-demineralizer inlet and the inlet to the reactor pressure vessel.

The conductivity sensors send signals to the operator about condenser leaks and demineralizer breakthrough, as well as information relative to overall rate of metal corrosion in the reactor cooling system.

When the absolute (actual) value of conductivity is required, the conductivity of pure water, 0.054 μmhos/cm, must be subtracted from the meter reading. This absolute value is required for comparison with the control values established by the vendor of the fuel (or to those established by the Nuclear Regulatory Commission).

The pH sensors signal when the acid/base balance in the coolant is disrupted. Improper values of pH can measurably enhance the corrosion process. For a BWR, the following maximum concentration of substances for reactor feedwater are typical of water quality during normal critical operations (Table 13-5-3).

TABLE 13-5-3
MAXIMUM WATER PROPERTIES IN A BWR

Water Property - BWR	Maximum Concentration - BWR
Dissolved iron & copper ions	< 30 ppb
Conductivity at 25°C (77°F)	< 0.1 µmho/cm
pH at 25°C (77°F)	7.0 (or slightly alkaline) (i.e., pH $\geq$ 7)
Dissolved oxygen	< 200 ppb

If the pH in the coolant were to increase to 8.7, according to Table 13-5-1, the corresponding conductivity value would increase to about 1.0 µmho/cm, or ten times the desired value. Thus, conductivity values serve as a check on pH values for BWR waters.

PRESSURIZED WATER REACTOR

With minor modifications, the locations and functions of sensors in a BWR apply to a PWR (Figure 13-5-7).

When primary water occasionally leaks into the secondary system, it carries several dissolved chemicals with it through the steam generator tubes, including:

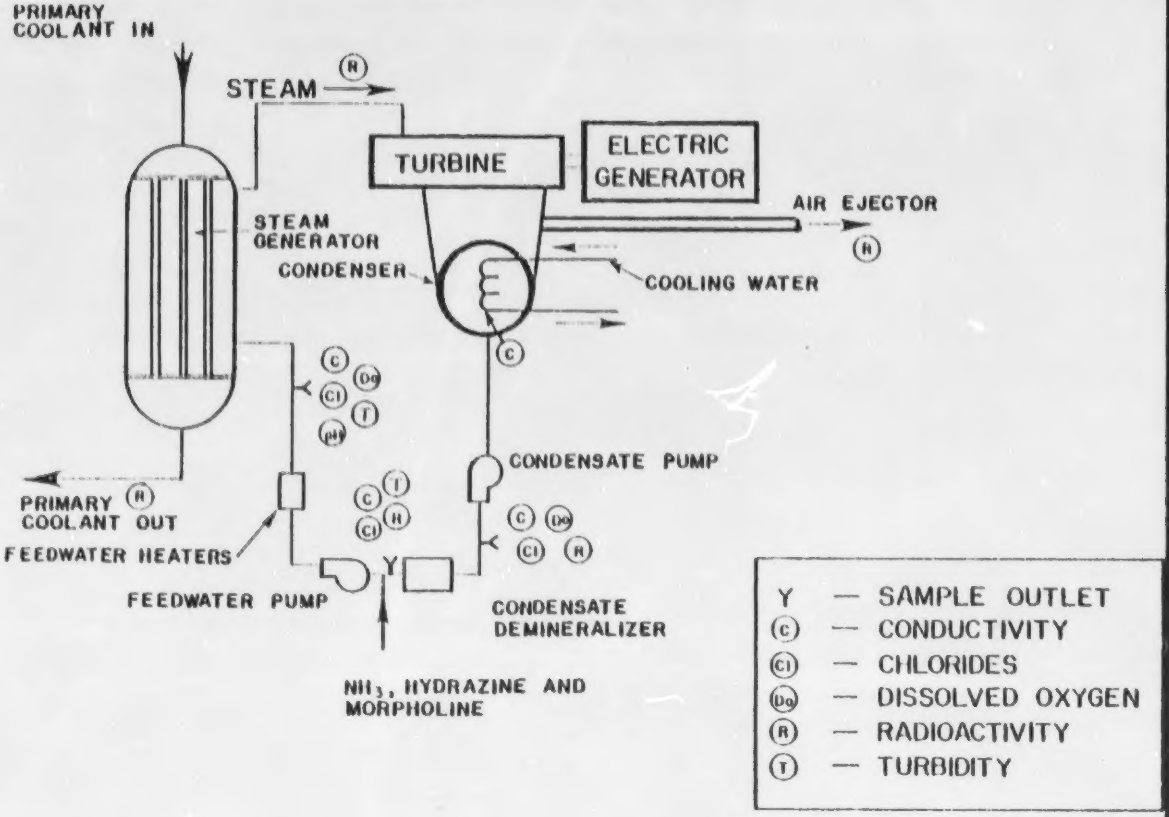

Figure 13-5-7 PWR once-through steam generator sampling points.

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Boric acid (used as a chemical shim).
Lithium-7 hydroxide (used to adjust the pH).
Radioactivity.

An increase of conductivity for this type of leak reflects an increase, mainly because of the hydroxide ion concentration, as can be deduced from Table 13-5-1.

When primary water leaks into a secondary system, radioactivity is also transmitted. Gamma radioactivity sensors, which monitor the secondary steam line, show a significant increase in output signal due to this activity. If the condensate demineralizer is working properly, its effluent should show very little (if any) radioactivity due to this leak. Radiation monitors (at the steam ejector, steam line and condensate pump) are activated by fission gas leakage from defective fuel elements. If combined activity, caused by activation and fission products that leak into the secondary, is sufficiently high, an alarm on the console is activated.

Several other features (Figure 13-5-7) are worth discussing. Although noncondensable gases are almost completely removed by air ejectors, several water-conditioning chemicals are still added. Morpholine (an ammonia derivative) is sometimes added to react with carbon dioxide, and hydrazine is added to react with oxygen. Both gases leak into the secondary system from the atmosphere. Some operators control the addition rate of these chemicals with automatic chemical analyzers. Turbidity analyzers monitor suspended solids levels at all times, just as in a BWR.

The secondary fluid is continuously recirculated (Figure 13-5-8), but there is no condensate demineralizer to remove suspended and dissolved impurities. Instead, a small portion (80 gal/min) of the circulating liquid is continuously removed to the liquid radwaste holding tanks, while exactly the same amount of make-up water is admitted into the loop. This arrangement keeps the volume of the circulating fluid constant. Cyclohexylamine may be added to control carbon dioxide levels, while sodium phosphate may be used to control pH between 8.2 and 9.0. Both of these water-conditioning chemicals are added to prevent formation of acidity, which would lead to rapid corrosion in the carbon steel steam generator and its associated piping. Monitoring instrumentation and sample points are very much like those discussed for preceding reactor types.

To further demonstrate the parallels between a BWR coolant loop and the secondary cooling loop of either type of PWR, the following (Table 13-5-4) maximum concentrations of substances in secondary water are typical. These values apply to a PWR (OTSG type) during normal critical operations, and should be compared to concentrations of similar substances in Table 13-5-3 for a BWR.

TABLE 13-5-4

MAXIMUM WATER PROPERTIES IN A PWR (OTSG)

Water Property - PWR Secondary	Max. Concentration - PWR
Dissolved iron & copper ions	< 22 ppb
Conductivity at 25°C (77°F)	0.1 µmho/cm
pH at 25°C (77°F)	9.5
Dissolved oxygen	< 20 ppb

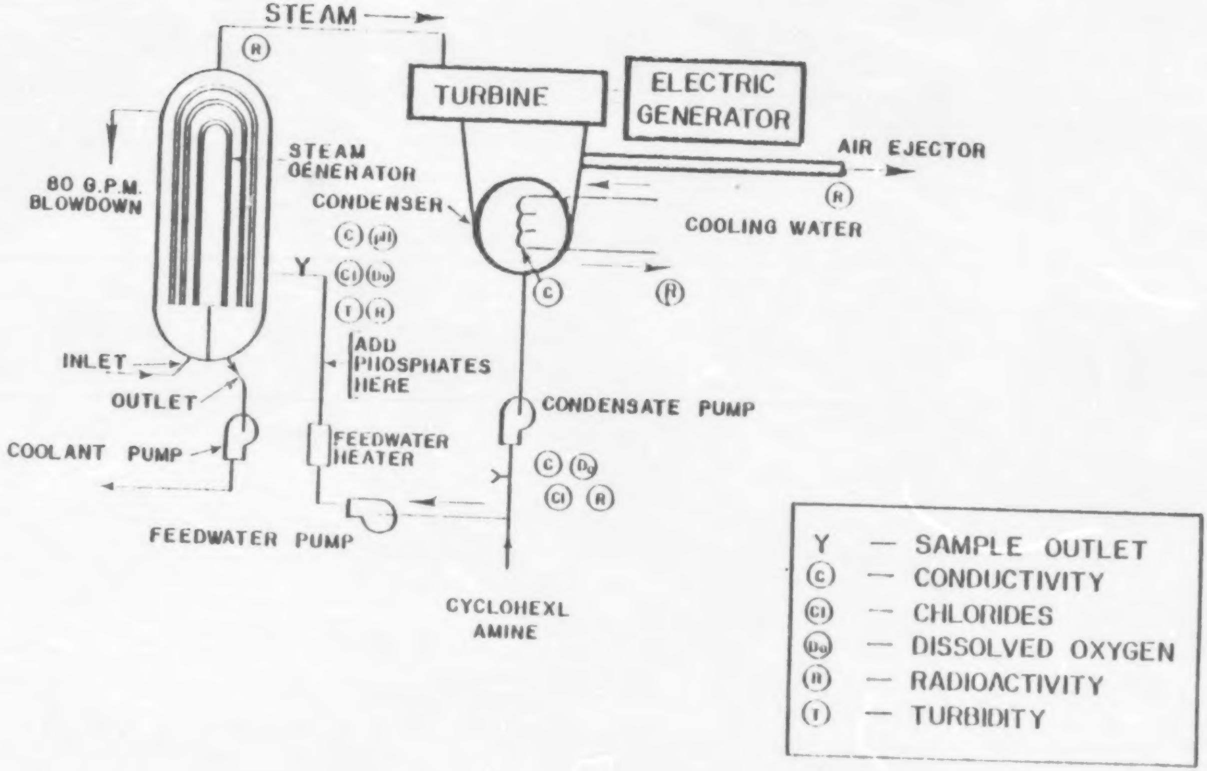

Figure 13-5-8. PWR (recirculating type) sample points for continuous, on-line monitoring.

EXERCISES

1. For solution, with pH of 10.0, in the steam generator of a PWR, calculate the following:
    a. Hydrogen ion concentration.
    b. Hydroxyl ion concentraion (if equilibrium constant:

$$K_w = (H^+) \quad (OH^-) = 10^{-14}).$$

2. During startup of a BWR, as temperature increases from 77°F (25°C) to 212°F (100°C), how much oxygen is released (boiled out) of solution?
3. An operator gets excess concentration alarms (simultaneously) from conductivity, chloride and oxygen sensors in inlet piping of condensate demineralizers. What is probable cause of the alarm?
4. Using data from conductivity table in this module, estimate expected conductivity value (in µmho/cm) if salt (NaCl) concentration increases ten times over its original value of 100 ppb.
5. What type of sensor (gamma-radiation or conductivity) should an operator use to estimate breakthrough on demineralizers? On ion-exchangers?

Parts 1 and 2, measurement of dissolved oxygen:

2	ring stands and 4 clamps.
1	tube of silastic sealer (or equivalent).
1	dissolved oxygen sensor (Yellow Springs Instrument Co., YSI 5739, or equivalent).
1	DO meter (YSI model 51-B or equivalent).
10	feet of signal cable (YSI 5740-10).
1	pump, centrifugal (polyethylene), (VMR Scientific, cat. no. 54902-000, or equivalent).
10	feet Koroseal tubing, or equivalent (5/8 in inner diameter)
4	hose clamps.
1	tank of oxygen gas (lecture size).
1	tank of nitrogen gas (lecture size).
1	plastic tubing to fit tank.
1	needle valve for flow control.
1	small clamp (to seal plastic tubing).
2	magnetic stirrers and stirring bars.
2	1000-ml beakers.
2	500-ml beakers.
1	g hydrazine to control oxygen.
1	12-tube, pyrex glass (4-5 mm inner diameter).
≃	64 in^2 aluminum foil, about 1/16 in thick.

Part 3, measurement of pH:

1	pH meter.
1	glass electrode.
1	reference electrode.
1	magnetic stirrer and stirring bar.
1	100-ml glass beaker.
1	thermometer, 0-100°C.
1	buret, 0-5 ml, in 0.1 ml increments (or equivalent).

10 ml of concentrated (36%) hydrochloric acid.
1 set standard pH buffer solutions.

Parts 1, 2 and 3:
Safety goggles.
Appropriate gloves and apron.

PROCEDURES

1. Construction of a closed-loop flow system:
    a. Preparation of pH electrodes -
        (1) With meter unplugged and in place on lab bench, check meter pointer to ensure that it is at center-scale, or at 7.0 on pH scale. If it is not, call lab assistant.
        (2) Plug in instrument; rotate function switch to "pH position."
        (3) Check solution levels in electrodes. (Solution in reference electrode should be higher than sample or buffer solution measured. Solution in reference electrode should have KCl crystals suspended in it.)
        (4) Hang reference and glass electrodes in electrode hanger attached to ring stand; connect their inputs to amplifier.
        (5) Immerse electrodes overnight in at least one-half inch demineralized water (in a 100-ml beaker).
        (6) Remove electrodes from beaker.

(7) Rinse electrodes (use demineralized water in a rinse bottle), blot dry with clean, soft tissue. (Do not touch tips of electrodes. A slight scratch can damage electrode permanently.

(8) Uncover filling hole on reference electrode.

b. Standardizing pH meter with buffer solutions -

(1) Rinse beaker and magnetic stirring bar with buffer solution (in range of pH to be measured); immerse electrodes in small amount of buffer solution for 10 seconds: dispose of solution in sink.

(2) Place beaker on magnetic stirrer and fill with at least one inch of buffer; measure temperature of buffer solution with thermometer; set "temperature compensating" switch to measured solution temperature.

(3) Start stirrer; immerse electrodes into buffer solution, coming no closer than 1 cm above magnetic stirrer.

(4) Rotate "standardize" control until meter pointer rests at correct buffer pH (meter is now adjusted for pH range of interest); store the electrodes in distilled water until used.

c. Assembling parts in a flow system -

(1) Connect about one foot of 5/8-inch tubing to each inlet and outlet port of water pump; connect other ends of tubing to apparatus (as illustrated in Figures 13-5-9 and 13-5-10). Use balance of tubing to connect beakers as shown in illustrations.

(2) Mount the pH electrodes into container (Figure 13-5-9).

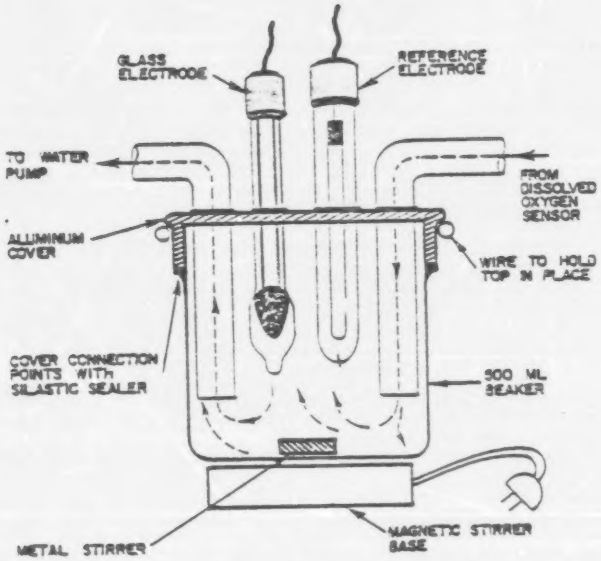

Figure 13-5-9. pH container inflow system.

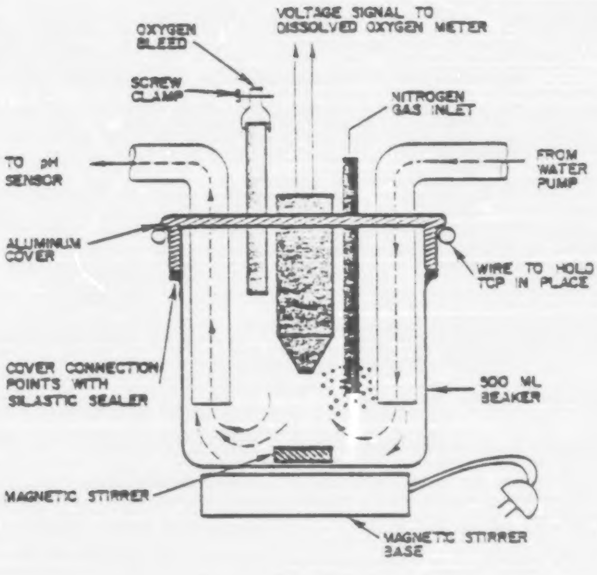

Figure 13-5-10. Measurement of dissolved oxygen (flowing water system).

(3) Seal all tubing and devices that penetrate aluminum cover (use silastic).

(4) If necessary, use wire to fix tubing to a 5/8-inch plastic pipe connector, which penetrates aluminum cover.

(5) Attach plastic tubing between nitrogen tank and nitrogen gas inlet; seal oxygen-bleed outlet with small diameter plastic tubing and small screw clamp.

(6) Fill both beakers, tubing and pump, which should require about 1000 to 1100 ml of oxygen-free water. This water may be prepared as follows:

CAUTION

OBTAIN ALL HYDRAZINE SOLUTIONS FROM INSTRUCTOR. SAFETY MUST BE OBSERVED WHEN HANDLING THIS MATERIAL.

(a) Add about 0.05 g hydrazine to about 1 liter of distilled water.

(b) Boil water for about 5 minutes; then cool to about 90°F; keep water level to top of container used for de-aeration step.

(c) Add water to flow system through open hole in the cover of apparatus (Figure 13-5-10) that eventually will house dissolved oxygen analyzer.

(7) Start water pump; remove any air bubbles that form in connecting tubing.

(8) Stop pump; insert dissolved oxygen monitor; seal connection with silastic.

2. Measurement of dissolved oxygen:
   - a. Turn on pH meter.
   - b. Turn on magnetic stirrer to create turbulence near all three electrodes.
   - c. Adjust pH meter to read pH.
   - d. Turn on DO meter.
   - e. Measure water temperature.
   - f. Set temperature-compensation dial to that temperature.
   - g. With selector knob on zero, adjust instrument to read zero ppm oxygen.
   - h. Move selector knob to "calib O_2;" adjust "calib" knob, if necessary.
   - i. Move selector switch to full-scale position; adjust "full-scale" knob if necessary.
   - j. Begin experimental phase by turning selector knob to read DO concentration of de-aerated water.
   - k. Connect oxygen tank to oxygen-bleed point (Figure 13-5-10); slowly bubble oxygen into solution at a pressure slightly above atmospheric pressure; record increases of concentration of DO with time on Data Table 13-5-1 (until negligible changes in concentration are observed).
   - l. Plot DO concentration (in ppm) on vertical axis (ordinate) of a sheet of linear graph paper; plot time (in minutes) on horizontal axis (abscissa).
   - m. Remove tubing connecting oxygen-bleed point and oxygen tank; be sure screw clamp is only slightly closed on bleed point plastic; slowly bubble nitrogen into oxygen-saturated water; observe decrease in dissolved oxygen level; record decreases

    on Data Table 13-5-2 (until negligible changes are observed).
  - n. Plot data on graph paper used in steps l and m.

3. Measurement of pH:
   - a. Record pH value in step c of part 2 on Data Table.
   - b. Through oxygen bleed point, add 0.1 ml of concentrated HCl with buret; record pH value on Data Table 13-5-3.
   - c. Add 0.4 ml more HCl; record pH.
   - d. Add 4.5 ml more HCl; record pH.

DATA TABLE 13-5-1

INCREASE OF OXYGEN

Time (minutes)	Oxygen Concentration (ppm)
0.0	

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DATA TABLE 13-5-2
DECREASE OF OXYGEN

Time (minutes)	Oxygen Concentration (ppm)
0.0	

DATA TABLE 13-5-3

pH of original solution (above)	
pH after addition of 0.1 ml HCl	
pH after addition of 0.5 ml HCl	
pH after addition of 5.0 ml HCl	

REFERENCE MATERIALS

Babcock & Wilcox Co. *Balance of Plant Criteria*, Document 36, Serial No. 3360, Rev. 1. New York: B & W, Nuclear Power Generation Division, September 1975.

Combusion Engineering, Inc. *Nuclear Steam Supply System Chemistry Manual*, CENPD-28, Rev. 2. Windsor, CT: Combustion Engineering, Inc., January 1976.

General Electric (GE). *BWR-6, General Description of a Boiling Water Reactor*, NEDP-20120. 14th ed. San Jose, CA: GE Nuclear Energy Division, April 1975.

Hicks, J. H. "Nuclear Steam Supply System Water Chemistry Research," TP1-11. Presented to the American Power Conference, Chicago, April 1971.

Hicks, J. H., and Bell, M.J. *Water Chemistry Manual for Standard Plants*, BAW-1407. New York: B & W, Nuclear Power Generation Division, December 1974.

Pocock, F.J. "Corrosion Control for Modern Central Station Steam Supply Systems," RDTPA-7613. Presented to the Symposium on Materials Performance and Power Plant Environments, October 1976.

1. Sketch and briefly explain the following:

   pH sensor.

   Conductivity sensor.

   Dissolved oxygen (DO) sensor.

   Halide ion sensor.

Turbidimeter.

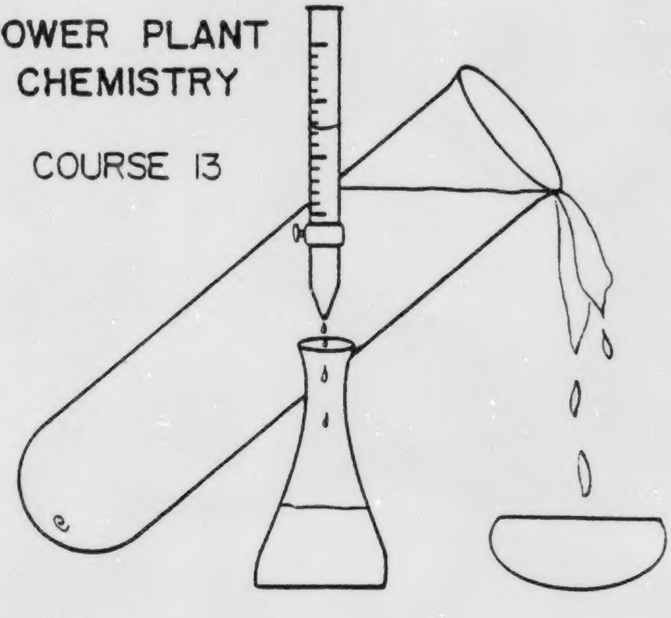
2. Describe why a halide detector system is used in a power plant water system:

3. Discuss, with aid of a sketch, how a DO meter is normally employed in a reactor water system:

NUCLEAR TECHNOLOGY

MODULE 13-6 WATER ANALYSIS FOR NUCLEAR POWER PLANTS. -

ROBERT B. NEEL



POWER PLANT
CHEMISTRY

COURSE 13

TERC-SW

TECHNICAL EDUCATION RESEARCH CENTER — SOUTHWEST
4201 LAKE SHORE DRIVE WACO, TEXAS

COURSE MODULES

COURSE 13 POWER PLANT CHEMISTRY

	MODULE 13-1	Water Quality Control
	MODULE 13-2	Raw-Water Treatment
	MODULE 13-3	Sources of Impurities in Reactor Water Systems
	MODULE 13-4	Water Treatment - Polishing by Ion Exchange, Evaporation and Demineralization
	MODULE 13-5	Water Properties Sensing
⇨	MODULE 13-6	Water Analysis for Nuclear Power Plants
	MODULE 13-7	Radioactive Waste Handling - Liquid and Gaseous

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INTRODUCTION

This module describes applications of wet-chemical analyses for similar, but discontinuous, monitoring of nuclear reactor solutions. Some are required and some are merely desirable, but all can be characterized as water quality analyses. In many cases, the techniques described in this module are used to calibrate or check continuous on-line sensor systems.

MODULE PREREQUISITES

The student should have completed all previous Modules in this Course.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. Define:
   - Continuous monitoring.
   - Grab sample.
   - Gravimetric analysis.
   - Colorimetric analysis.

    - Flame-emission analysis.
    - Radiochemical analysis.
2. Describe major chemical sampling techniques used at nuclear power plants.
3. Describe general principles involved in the following types of chemical analyses:
    - Gravimetric.
    - Colorimetric.
    - Volumetric.
    - Flame.
    - Radiochemical.
4. State reasons for collecting chemical and radiochemical samples from the following:
    - Purification system.
    - Steam generator system (pressurized water reactor).
    - Other miscellaneous systems (e.g., evaporator demineralizer, high-activity waste tank and evaporator distillate).
5. Titrate boric acid in the presence of mannitol; show data conversion.

Continuous monitoring of water properties is performed automatically by special monitors (for liquids and gases) in a reactor water system. This monitoring takes place 24 hours a day, 365 days a year. Most take samples of liquids, which are usually cooled to below 115°F (43°C) and depressurized before sampling (to protect analytical instruments).

Grab samples also are taken from reactor water systems. A grab sample is "grabbed" at a specific sampling location, at some specified time, for later analysis in a chemical laboratory. For example, a chloride ion sample might be taken daily between 8:00 and 9:00 a.m. at the effluent point on a condensate demineralizer in a BWR. Grab samples may be obtained in any form: solid, liquid or gaseous. They are taken at both high and low temperatures and pressures. Many types of grab samples are taken because no other method is appropriate or available.

Most samples taken from reactor systems are grab samples. Many analyses of reactor water systems are needed only infrequently, and continuous analyzers are not economical under these conditions.

When taking a grab sample from a reactor water system, several precautions should be taken. The sampling arrangement should be organized so that the time involved in obtaining the samples is minimized, that they are not modified (e.g., by impurities) and that the individuals who take these samples are protected at all times from high pressures, extreme temperatures, and radioactive materials.

To prevent cross-contamination of samples with radioactivity, the laboratory at a nuclear power plant is usually divided into four distinct areas:

- High-radioactivity area.
- Low-radioactivity area.
- Counting room.
- Environmental analysis area.

The latter is frequently physically separated from the other three sections, which, by necessity, are usually close in proximity to the containment vessel.

LIQUID SAMPLES TAKEN AT HIGH TEMPERATURES AND PRESSURES

Samples may be collected directly, in a centrally located sample hood, from the primary coolant system of a PWR (Figure 13-6-1). Three points are generally sampled:

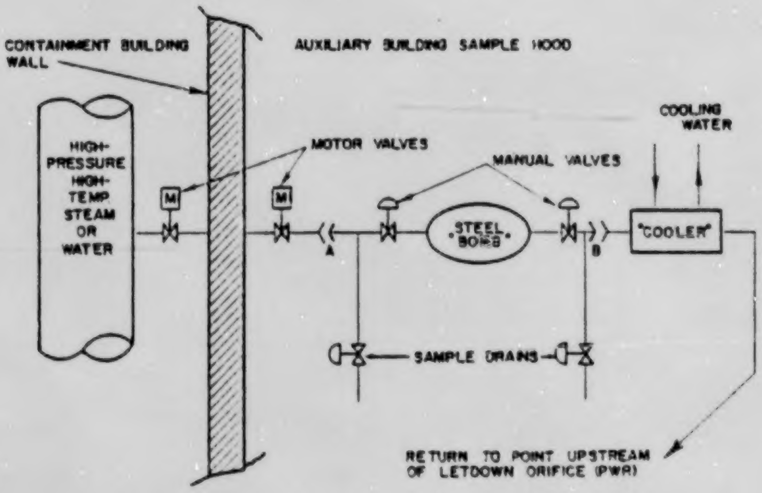
CONTAINMENT BUILDING WALL
AUXILIARY BUILDING SAMPLE HOOD
HIGH-PRESSURE HIGH-TEMP STEAM OR WATER
M
M
MOTOR VALVES
MANUAL VALVES
COOLING WATER
A
STEEL BOMB
B
"COOLER"
SAMPLE DRAINS
RETURN TO POINT UPSTREAM OF LETDOWN ORIFICE (PWR)

Figure 13-6-1. High-temperature, high-pressure sampling system for nuclear reactor.

Reactor coolant water.
Pressurized steam.
Pressurized water.

To take samples from these primary systems, the motorized valves are first closed. Then the stainless steel sampling container, or "bomb," is connected to the manual sampling valves at points "A" and "B." The manual sampling valves and sample drain valves must be closed because the bomb is evacuated (to prevent contamination by the atmosphere). When all connections are tight, the manual valves are opened, followed by opening of the motorized valves leading from the primary system to be sampled. A liquid sample is flushed through the sample lines and sample container to clean them, then cooled and returned to a point upstream of the letdown orifice. After flushing the system for about ten sample volumes, the electric motor valves are closed to seal off the primary. Next, the manual valves are closed to seal the sample container. The sample drain valves are then opened to relieve pressure between the manual and motorized valves. The sample is allowed to cool, and removed to the laboratory for analysis.

The method described above is used routinely to collect samples for total dissolved gas analysis. Total dissolved gases may include:

Hydrogen.
Nitrogen.
Radioisotopes (of xenon, krypton, nitrogen, iodine and argon).

After collection, the sample is removed to the laboratory where it is allowed to de-gas, if liquid, into a known, evacuated volume-measuring system. Pressure of the gas (above the solution) is measured. From this pressure, total gas concentration in a sample can be calculated: system pressure is reduced to atmospheric conditions; gas mixture is recirculated through a hydrogen analyzer; dissolved hydrogen gas concentration is then determined.

Liquid samples and steam samples are collected from the PWR pressurizer by using the techniques discussed (Figure 13-6-1). With little modification, these same techniques may be used to sample boiler water or steam in a BWR.

LIQUID SAMPLES TAKEN AT LOW TEMPERATURES AND PRESSURES

Most liquid samples are routinely taken at moderately low temperatures and pressures because these samples may be handled more safely and conveniently. Samples are generally taken in a centralized sample hood facility. The low temperatures and low pressures in the samples result from careful selection of points at which samples may be taken (in either a BWR or a PWR). In a PWR (Figure 13-6-2), most samples are taken at points S-2, S-3 and S-4. At each of these points, the hot, pressurized primary water has been cooled and depressurized by the letdown cooler and letdown orifice.

In a BWR (Figure 13-6-3), samples are taken from condensed and depressurized steam at sample points S-1, S-2, S-3 and S-4. At some of these points, continuous monitors may also be stationed. For the BWR, these are identified by a circle surrounding abbreviation of monitor type.

Samples of crud in a PWR may be taken at sample point

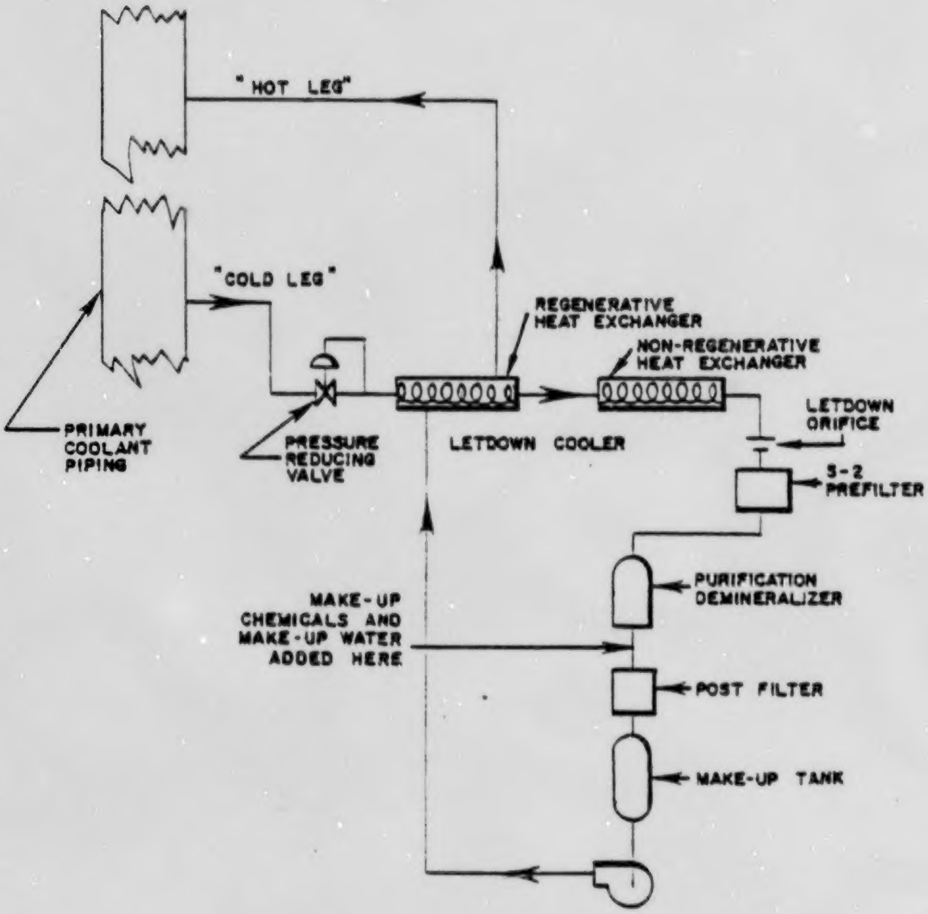
"HOT LEG"
"COLD LEG"
REGENERATIVE HEAT EXCHANGER
NON-REGENERATIVE HEAT EXCHANGER
LETDOWN ORIFICE
PRIMARY COOLANT PIPING
PRESSURE REDUCING VALVE
LETDOWN COOLER
S-2 PREFILTER
PURIFICATION DEMINERALIZER
MAKE-UP CHEMICALS AND MAKE-UP WATER ADDED HERE
POST FILTER
MAKE-UP TANK

Figure 13-6-2. PWR chemical purification system grab sample points.

S-2 (Figure 13-6-2). For example, several liters of coolant water may be pulled through a 0.45-micrometer Millipore plastic membrane (or equivalent) filter at velocities sufficiently high to keep larger particles suspended in sample line. When sampling, holding tanks for suspended solids,

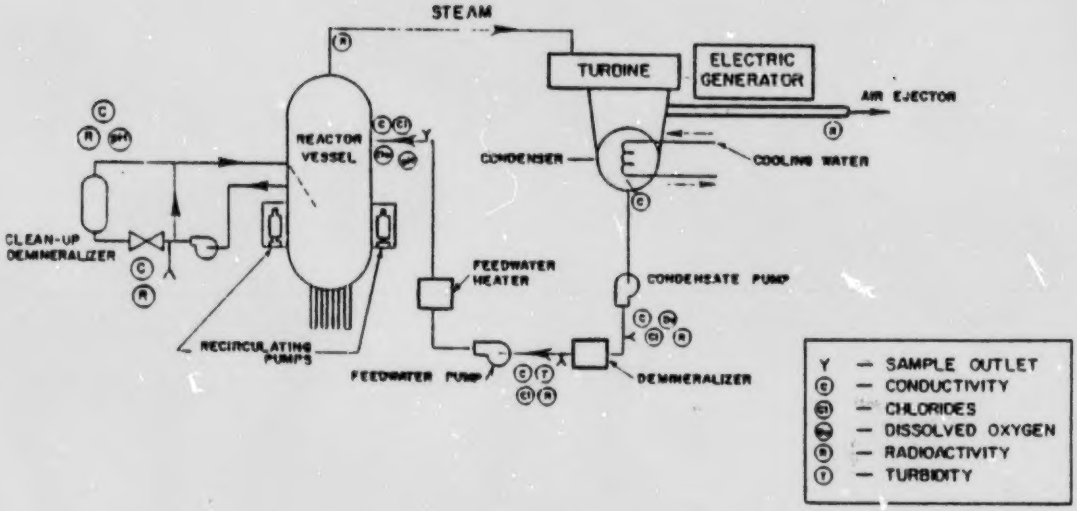

Figure 13-6-3. BWR sample points for continuous, on-line monitors and grab samples.

sample velocity must be maintained high enough to prevent settling of larger particles. For this purpose, the tanks have a recycle pump, which should be turned on for several minutes before sampling.

A sample is usually taken daily, in both a PWR and a BWR, for dissolved oxygen in reactor coolant (or feedwater), by using a sample tube (Figure 13-6-4). Glass nipples on the tube are connected by low-pressure tubing to sample point and high-activity waste drain. In a PWR, this sample is taken at point S-2 (Figure 13-6-2); and, in a BWR, at sample point S-1 (Figure 13-6-3). After sample lines have been flushed and samples collected, they are taken to a laboratory for analysis by titration, as discussed later in this module.

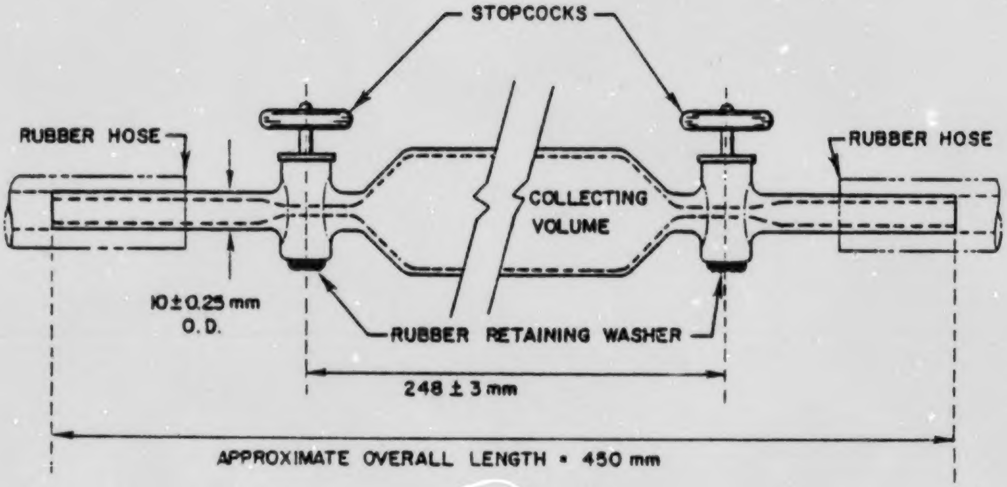

Figure 13-6-4. 500-ml sample tube for dissolved oxygen determination (glass).

For this type of low-pressure, low-temperature liquid sample, some of the other important systems involved include:

Spent fuel.
Liquid radwaste.
Evaporator (bottoms and distillates).
Demineralizer effluents.
Circulation pump discharge (steam generator of a PWR).

GASEOUS SAMPLES AT LOW TEMPERATURES AND PRESSURES

The samples of gas are pumped from their sources to the central sampling station for collection in glass bulbs

(Figure 13-6-4). Because they may contain radioactive gases, they are best collected in a fume hood. Typical sources of low-pressure gases that require analysis include:

Condenser off-gas, in a BWR.
Vents from various operating systems.
Waste hold-up tanks, liquid and gaseous.

GENERAL PRINCIPLES OF SAMPLE ANALYSES

Sample analyses in a power plant laboratory are conducted by both physical and chemical methods. The major physical methods (pH, conductivity and turbidity) were discussed in Module 13-5. Most chemical analyses, however, are of the wet-chemical type. The routinely used wet-chemical techniques discussed in this section include:

Titration.
Spectrophotometry.
Flame emission.
Gravimetric analysis.
Radiochemical.

GRAVIMETRIC ANALYSIS

Gravimetric analysis is used to determine the mass of solids (crud) suspended in a given volume of reactor coolant solution. A solids sample, collected on a 0.45-micrometer pore plastic membrane filter, may be weighed to find its solids content. Reduction in intensity of light transmitted through the filter can be used as a very crude measure of suspended solids.

COLORIMETRY - SPECTROPHOTOMETRY

The most frequently employed method of chemical analysis, colorimetric analysis, involves a measurement of the amount of light absorbed or transmitted by a sample as a function of color (i.e., the frequency or wavelength of light). The principles involved may best be understood from a schematic representation of a common laboratory colorimeter (Figure 13-6-5). All of the more complex spectrophotometers contain functioning parts similar to those shown. The source of radiant energy (1) produces light of all col-

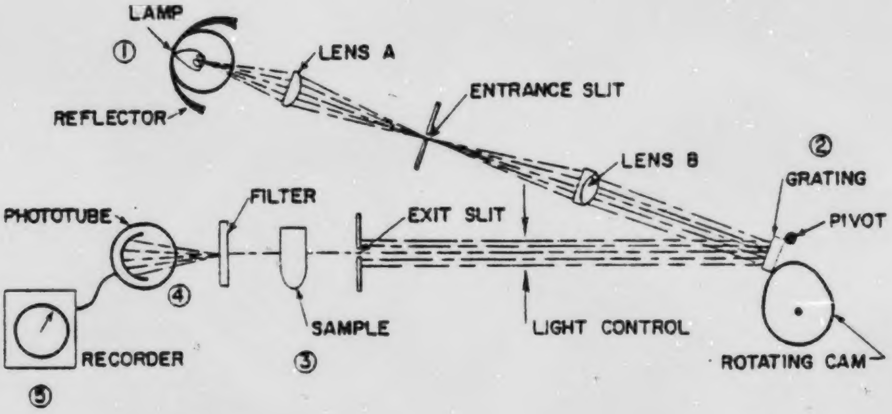

Figure 13-6-5. Laboratory colorimeter.

ors, which is broken into a rainbow of colors by the grating (2). By moving the cam attached to the grating, selected wavelengths of colored light are allowed to enter the exit slit and the sample to be analyzed (3). The phototube (4) detects any reduction in light intensity as it passes through the sample, which absorbs some of the light. The meter (5) indicates this reduction in light intensity in the sample. The filter just improves phototube selectivity for light transmitted through the sample.

A measurement of the concentration of a particular substance in a sample involves formation of a specific color with a special chemical reagent. Depth of the color formed is usually proportional only to the quantity of the specified chemical element being measured.

The color-forming reagent is usually an organic compound, which forms a stable compound with the desired element to be analyzed. For example, in a determination of iron in industrial water, a solution of orthophenanthroline, when added to sample to be tested, produces an orange-red color, the depth of which is proportional to the amount of ferrous iron in the water.

The proper color of light to use for this analysis has a wavelength of 510 millimicrons (i.e., it is colored approximately blue-green). This light color entering the sample has been demonstrated to give the greatest reduction of light transmission when passed through an orange-red solution.

Spectrophotometric analyses are routinely carried out on reactor system samples for the following:

Chloride ion.
Fluoride ion.
Dissolved oxygen.
Phosphate.

Iron.

Hydrazine.

Results of analyses for chloride, fluoride and dissolved oxygen are compared with control standards, which must not be exceeded if reactor metal corrosion is to be prevented. Iron analysis is an index of corrosion of steel (in a reactor), which is composed primarily of iron.

Phosphate and hydrazine values are associated with control of pH and oxygen concentrations, respectively, in the water of a steam generator in a PWR. If these concentrations are not correct, undesirable corrosion rates may occur.

FLAME-EMISSION ANALYSIS

Sodium and lithium ions are commonly measured by a flame-emission analysis. Sodium ion is an undesirable impurity in reactor water systems because it becomes radioactive when it passes through a reactor core. Lithium ions are used for pH control in PWR's to prevent corrosion problems. A sample to be analyzed is prepared in solution form and sprayed (under controlled conditions) into a hot flame. Atoms in the molecule absorb energy from the flame and become excited. They re-emit this thermal energy in the form of light, the specific color of which is peculiar to the emitting atom.

The more atoms present in a sample, the greater the intensity of re-emitted light. Concentration of a substance in the sample is proportional to intensity of emission of a specific frequency of light by the flame (Figure 13-6-6). Note similarity of this flame photometer to the spectro-

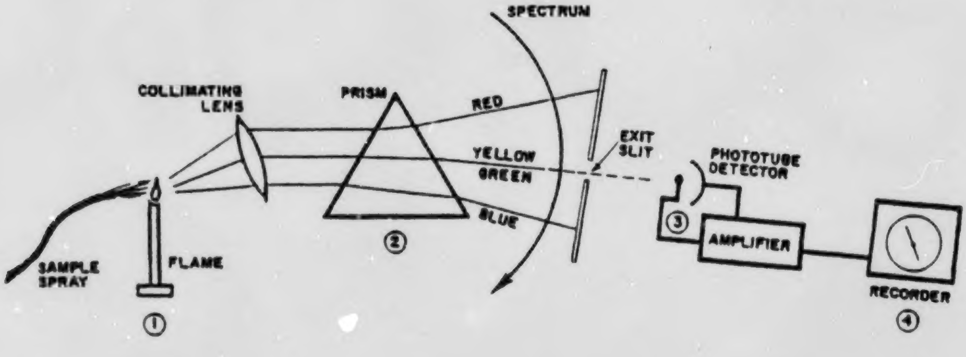

Figure 13-6-6. Flame photometer.

photometer (Figure 13-6-5).

The flame (1) substitutes for the lamp as a source of light. Some means, such as a prism (2), is needed for selecting only the specific colored light (wavelength) from the many colors produced in the flame. After sorting the colors, the desired color is passed through a slit (the others are stopped by the slit body), and its intensity is measured by the phototube detector (3). The amplifier is necessary to magnify signal current so that it will be sufficiently strong to move a meter needle (4).

A modification of flame analysis, called atomic absorption spectroscopy, is rapidly gaining widespread acceptance and use. In this use, the flame vaporizes and excites the sample, but the light source is a lamp emitting wavelengths of light specific to the element being analyzed; e.g., a sodium lamp is used for determining sodium concentrations. Sensitivity and specificity are greatly increased, allowing determination of very low concentrations. (This analytical technique is also called "atomic resonance spectroscopy.")

ANALYSIS BY TITRATION

In a titration, a known concentration of a standard chemical (reagent) is added, in solution form, to an unknown quantity of the substance being determined in a sample, also in solution form. Reagent is added to the solution until the sample is completely reacted. Organic dyes are generally used as indicators of the completion of the reaction. When the unknown quantity of a substance is depleted, the dyes react with the excess reagent and change color. This method is not as sensitive as the others because many more atoms are required to produce a visible dye color change than to show a change in light intensity (as in a spectrophotometer). The main advantages of titration are 1) it is rapid and 2) it is inexpensive.

A common example of a titration is determination of gaseous oxygen amounts dissolved in reactor coolant (or feedwater). A sample is collected in a glass sample bulb (Figure 13-6-4) and then analyzed by the Winkler method. In this method, the sample is treated with chemicals while in the bulb, before titration, to produce an amount of iodine chemically equivalent to the amount of oxygen dissolved in the sample. The iodine is then titrated with a chemically equivalent amount of sodium thiosulfate solution. The quantity of thiosulfate solution is measured as equivalent to the amount of iodine produced, and the amount of iodine produced is equivalent to the amount of oxygen initially present in the sample.

This titration, indirectly, measures oxygen concentration in reactor water. Other titrations, common in a power plant laboratory, include those for chromates (used as a corrosion inhibitor in some cooling waters), phosphate (sometimes used to control pH in the steam generator of a PWR) and boric acid (used in a PWR as a neutron control mechanism).

RADIOCHEMICAL ANALYSIS

The most common forms of radiochemical analysis are measurements of gross beta and gross gamma activity in a sample. (The word "gross" means that the activity from the individual nuclides in a mixture remains unknown, but the total activity of the mixture is determined.)

If, for example, an analysis of radioactivity of a specific radionuclide is necessary, it may be accomplished by radiochemical spectroscopy. Gamma rays from a mixture of radionuclides are detected and signals from the detector output are resolved by analysis of energy spectrum into their separate nuclide activities.

The most common types of detectors used are solids. The techniques used in radiochemical analysis are discussed in another Course in this series.

ROUTINE TYPES OF ANALYSES AT POWER PLANTS

Tables 13-6-1 and 13-6-2 summarize the most common types of analyses performed in power plant laboratories (the more common analyses are listed first; the least used analyses are listed last). Some analyses are used as indicators for control of solution parameters; other analyses

TABLE 13-6-1

CHEMICAL ANALYSES IN NUCLEAR POWER PLANT LABS

Type of Analysis	Method and/or Instruments Used
Boric Acid	Titration
Chlorides	Spectrophotometric
Fluorides	Spectrophotometric
pH	pH meter
Dissolved oxygen	Modified Winkler, titration, indigo carmine, colorimetric
* Lithium	Flame emission
Turbidity	Turbidimeter
Chromates	Titration
Total dissolved solids	Gravimetric
Conductivity	Conductivity cell and bridge
* Hydrazine	Spectrophotometer
* Phosphate	Spectrophotometer
Sodium	Flame emission
Iron	Spectrophotometer
Dissolved hydrogen/dissolved gas	Gas sampling rig, thermal conductivity
Filterable crud	Crud filter, balance
Noncondensables (N_2, H_2, Ar)	Gas sampling rig
Oxygen in gas	Gas partitioner (chromatographic)
Hydrogen in gas	Gas partitioner (chromatographic)
Suspended solids	Crud filter, millipore comparison chart

* Peculiar to a PWR.

TABLE 13-6-2

RADIOCHEMICAL ANALYSES IN NUCLEAR POWER PLANT LABS

Type of Analysis	Counting Method
Gross beta	Liquid scintillation
Gamma spectra	Ge(Li) spectroscopy
Tritium	Liquid scintillation
Iodine (vapor)	Ge(Li) spectroscopy
Particulate	Ge(Li) spectroscopy
Strontium	Beta - proportional counting
Iodine (liquid)	Ge(Li) spectroscopy
Cesium	Ge(Li) spectroscopy
Barium-Lanthanum	Ge(Li) spectroscopy
Gross alpha	Alpha - proportional counting
Gross gamma	NaI scintillation
Fluorine-18	NaI scintillation

are used only as indicators of corrosion or other potential problem areas.

CHEMICAL SAMPLING AND ANALYSIS OF THE CIRCULATING COOLANT

Chemical samples are normally taken at the same frequency and at the same sampling points when the reactor is subcritical (such as during startup or shutdown) as during normal critical operations. The reason for these nearly identical procedures is that the corrosion processes monitored by the samples are essentially the same for both conditions. From a corrosion standpoint, the most significant difference is temperature. Higher temperatures mean, chemically, a more rapid rate of attack for the corrosion processes. On the other hand, when a reactor is in an outage (such as during refueling), the reactor vessel is interconnected to the fuel-handling system; both systems are depressurized and exposed to the atmosphere; thus, during refueling, no gas samples are taken for gases dissolved in reactor water. (The only gas samples are those that monitor the atmosphere for radioactivity in the working areas and in the off-gas systems.)

Table 13-6-3 summarizes the types of chemical samples routinely taken from a nuclear reactor water system during various modes of operation. The sampling frequency for each sample may vary somewhat at different installations. The values listed are common frequencies (suggested by reactor vendors) for a nuclear steam supply system. These analyses apply to both PWR and BWR, except where otherwise indicated.

Examine samples taken for a PWR. Concentration of

TABLE 13-6-3

TYPICAL ROUTINE CHEMICAL SAMPLES FROM A NUCLEAR REACTOR

Type of Sample	Frequency	Operating Mode		
		Critical	Subcritical	Refueling
Turbidity	Daily	X	X	X
Crud	Weekly	X	X	-
* Boric Acid	Daily	X	X	X
* Lithium	Daily	X	X	-
pH	Daily	X	X	-
Dissolved O_2	Optional	-	-	-
Chlorides	Daily	X	X	X
Fluorides	Daily	X	X	X
* Dissolved H_2	Weekly	X	X	-
* Total Gas	Weekly	X	-	-
Sodium	Optional	X	-	-
Gross Gamma	Daily	X	X	X
Gross Beta	Daily	X	X	X
$^{133}I/^{131}I$	Weekly	X	X	X
^{89}Sr, ^{90}Sr	Weekly	X	X	X

* Peculiar to a PWR.

boric acid directly adds negative reactivity to the reactor core. As fuel reactivity decreases, boric acid concentration reduces gradually. Wet-chemical analysis is the primary indicator employed to ensure that reduction in boric acid has been correctly accomplished. Lithium hydroxide is used to adjust pH, as nearly as possible, to neutral at operating temperatures (to minimize corrosion of reactor metals). The pH must be tested to ascertain that a proper amount of lithium hydroxide has been added for adjustment of basicity. A total gas sample is used to be sure that gas concentration remains below level at which gas pockets are known to form in a primary system. Dissolved hydrogen is used to maintain oxygen level at essentially zero concentration in a primary system. The partial pressure of hydrogen in total dissolved gas must be adjusted if a proper amount of hydrogen is to be available for reaction with dissolved oxygen.

The remaining chemical samples apply to both a BWR and a PWR.

Dissolved oxygen and chloride ions are monitored because a buildup of these elements can lead to serious metal failure by stress-corrosion cracking. Fluoride concentration also must be controlled because it may lead to serious corrosion of zirconium alloy used as cladding for the fuel. The pH should be neutral (or slightly basic) to minimize uniform corrosion of reactor steel.

Turbidity is an instantaneous index of the relative amount of suspended solids (crud) floating through a reactor core. The absolute amount of crud floating in a coolant is an index of corrosion rate (under normal operating conditions).

Sodium may leak into a system from condenser tubes or during regeneration of ion exchangers. It may become radioactive as it passes through a reactor core region and create a personnel hazard later if not completely removed.

The remaining samples are analyzed by radiochemical methods. Gross gamma and gross beta analyses help assess potential radiation hazards to maintenance and operations personnel. This information, along with data from the difficult ^{89}Sr/^{90}Sr analysis, is important in assessing amounts of dilution water necessary for safe disposal of liquid waste.

An analysis of ^{133}I and ^{131}I may be used as a sensitive indicator of small fuel leaks. If a serious fuel cladding defect occurs, radioactivity in the reactor coolant increases quickly. If a pinhole leak occurs in the fuel cladding, buildup of radioactivity in the coolant may be indistinguishable from normal day-to-day variations. A gradual increase in coolant activity, due to a number of small cracks in one or more fuel elements, may be mistaken for gradual buildup of activity in coolant due to tramp uranium (Figure 13-6-7).

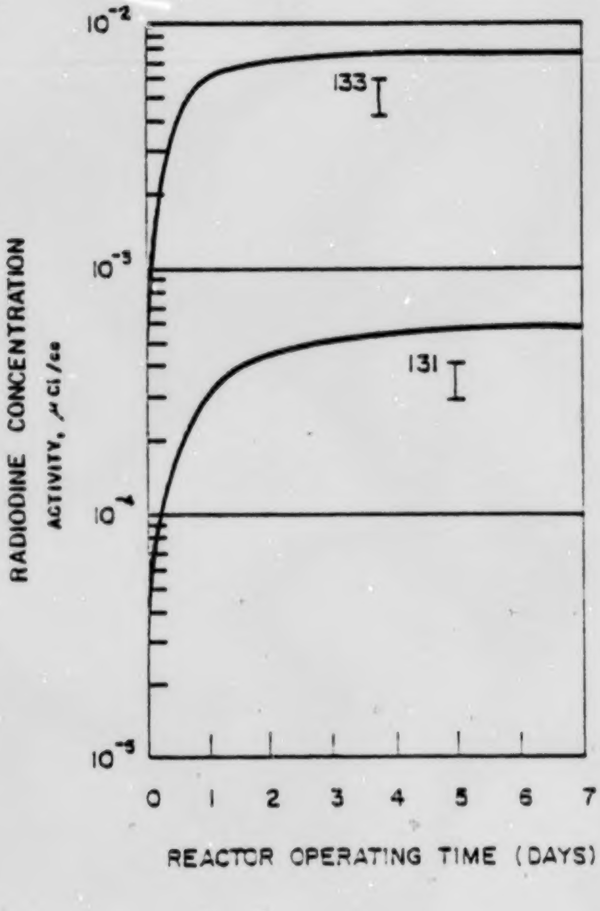

Figure 13-6-7.
Gross radioiodine expected in reactor coolant from surface contamination of fuel elements.

At steady-state reactor operation, with a constant number of fuel cracks, the ratio of ^{133}I to ^{131}I, from contamination, is roughly 14:1. When the number of fuel defects increases, the ^{133}I to ^{131}I ratio may decrease to a value as small as 1.5:1; the reason for this decrease is that the ^{133}I must diffuse out of the fuel into the coolant, which takes time. During this time, the ^{133}I decays more rapidly (half-life of 21 hours) than the ^{131}I (half-life of 8 days), producing a decrease in the ratio.

CHEMICAL SAMPLING AND ANALYSES OF OTHER KEY REACTOR WATER SYSTEMS

To determine effectiveness of a purification (cleanup) system in removing radioactive materials, corrosion products and other chemicals from circulating coolant, the outlet (effluent) of the purification demineralizer must be routinely sampled. A weekly sample is usually adequate to determine that demineralizers are working properly in any operating mode; however, a daily effluent sample, which is subsequently monitored for gross gamma contamination, serves as an early warning of breakthrough of demineralizer resins.

In a PWR, in addition to the primary system, the steam generator system water must be sampled and analyzed. Monitoring this secondary system is similar to that of a BWR (the steam generator is also a boiler). Table 13-6-4 lists types of samples to be taken, and sampling points, for analyses of feedwater in a steam generator. Total solids analyses are necessary to ensure that solid content remains low in the circulating secondary coolant. Dissolved oxygen is measured because of its corrosion potential. Hydrazine is added to reduce oxygen level beyond that provided by the

TABLE 13-6-4

TYPICAL STEAM GENERATOR FEEDWATER SAMPLING POINTS

Sample Type	Sample Point
Total solids	At outlet of last feedwater stage
Dissolved Oxygen	De-aerator outlet
Hydrazine	Downstream of point of addition
Total silica (as SiO_2)	Downstream of polishing demineralizers
Total iron (as Fe)	At outlet of last feedwater stage
Total copper (as Cu)	Downstream of polishing demineralizers
pH at 77°F (25°C)	Condenser hotwell and outlet of last feedwater heater stage
Conductivity	Condenser hotwell and outlet of last feedwater heater stage

air ejectors on the condenser. Optimum pH (for minimum corrosion) must be monitored with grab samples (or continuous analyzer).

Other reactor systems sampled and later analyzed include:

Distillate and bottoms from waste evaporators.
Collection tanks for evaporator distillate, which is condensed and stored for reuse as makeup water.
Low- and high-level radioactive waste tanks.
Spent resin storage tanks.
Makeup water.

The types of samples needed (and their frequency) for these systems depends upon the ultimate fate of the liquids involved. The quantity of chloride ions must be carefully regulated in these tanks because most of them are stainless steel, which can corrode in the presence of these ions and oxygen. A waste-liquid tank can be emptied, but it must be sampled and analyzed before discharge into environmental liquids, such as lakes or rivers.

Thus, water analysis is an extremely important method for evaluating the correct, efficient and safe operation of a nuclear power plant.

EXERCISES

1. When sampling waste tanks that contain solids, the recycle pump continues to run. If this pump breaks down, but a sample is taken anyhow, would the analysis error be high or low? Why?
2. If the reagent in a titration is accidentally prepared twice (2X) as strong as the procedure calls for, how much would the results be in error?
3. A lab analyst, in reporting the results of a $^{133}I/^{131}I$ analysis, accidentally sent out the ratio $^{131}I/^{133}I$ to the shift supervisor. How would an alert supervisor detect this error?
4. What might be the best interpretation of the following chemical analyses for samples taken in a BWR: turbidity - 3X normal value; crud - normal value?

MATERIALS

1 25-ml Erlenmeyer flask.
1 50-ml pipette.
1 25-milliliter (ml) pipette.
1 50-ml buret.
4 500-ml volumetric flasks for preparation of boric acid solutions.
1 1000-ml volumetric flask for preparation of NaOH reagent.
1 analytical balance, sensitive to about ± 10 mg (such as the OHAUS 310).
1 plastic ampule containing carbon-dioxide-free sodium hydroxide to give 0.100N NaOH when diluted to exactly 1.00 liter of solution (J.T. Baker Dilut-it JT4687-1 or equivalent).
10 grams of mannitol; Fisher reagent grade D mannitol may be used without purification.
100 ml of ethyl alcohol.
2 grams of phenolpthalein indicator solution.
Demineralized or distilled water.
1 set of safety goggles, gloves and apron.

PROCEDURES

1. Solutions to be prepared:
   a. Use distilled water; open sealed ampule of concentrated NaOH and wash into a 1-liter volumetric flask (as instructed by manufacturer); fill flask

with water to 1-liter mark. (Note: Exact normality of solution is 0.100N NaOH.)

   b. To prepare solutions of boric acid for titration, dissolve reagent-grade boric acid of the following weights in 500-ml volumetric flasks:

      3 grams.
      5 grams.
      7 grams.
      9 grams.

   Dissolve the solids in distilled water, and add distilled water up to the mark on each flask. Concentration of solution for titration in each flask is approximately as follows: 3000, 5000, 7000 and 9000 ppm of boric acid, respectively.

   c. Add one gram of reagent-grade phenolpthalein in 50 ml of ethyl alcohol and dilute to about 100 ml with demineralized water.

2. Titration of boric acid.
   a. Pipette a 25-ml sample of the 9000-ppm boric acid solution into a 250-ml Erlenmeyer flask; add about 5 grams of mannitol and 3 to 5 drops of phenolpthalein indicator solution.
   b. Fill clean 50-ml buret with 0.10N NaOH solution; slowly add base to flask with swirling motion until colorless solution just becomes (and remains) pink - this is the end point; repeat steps a and b in another sample of the 9000-ppm boric acid solution to obtain a duplicate determination; record on Data Table 13-6-1 milliliters of base used for each determination.
   c. Repeat steps a and b for each of the other boric

acid solutions (7000 ppm, 5000 ppm and 3000 ppm); record milliliters of base used for each determination on Data Table 13-6-1; calculate averages for each concentration; record on Data Table 13-6-1.

DATA TABLE

DATA TABLE 13-6-1
BORIC ACID DETERMINATION

Boric Acid Samples	0.100N NaOH (Base) Used
9000 ppm	______________ ml
9000 ppm	______________ ml
average	______________ ml
calculated ppm*	______________ ppm
7000 ppm	______________ ml
7000 ppm	______________ ml
average	______________ ml
calculated ppm*	______________ ppm
5000 ppm	______________ ml
5000 ppm	______________ ml
average	______________ ml
calculated ppm*	______________ ppm
3000 ppm	______________ ml
3000 ppm	______________ ml
average	______________ ml
calculated ppm*	______________ ppm

*1. Calculate actual concentration of H_3BO_3 from the following formula:

$$\text{ppm } H_3BO_3 = \frac{(\text{ml base})\ (\text{normality of base})\ 61{,}830}{\text{ml sample}}$$

61,830 is a conversion factor the derivation of which is shown in the appendix.

2. Write chemical reaction for titration:

$H_3BO_3 + NaOH \rightarrow$ ______________ + ______________.

REFERENCE MATERIALS

Babcock and Wilcox Co. Balance of Plant Criteria, Document 36, Serial No. 3360, Rev. 1. New York: B and W, Nuclear Power Generation Division, September 1975.

Combustion Engineering, Inc. Nuclear Steam Supply System Chemistry Manual, CENPD-28, Rev. 2. Windsor, CT: Combustion Engineering, Inc., January 1976.

Dow Chemical Company. Chemical Processing by Ion Exchange. Midland, MI: Dow Chemical Co., 1976.

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Pocock, F.J. "Corrosion Control for Modern Central Station Steam Supply Systems," RDTPA-7613. Presented at the Symposium on Materials Performance and Power Plant Environments, October 1976.

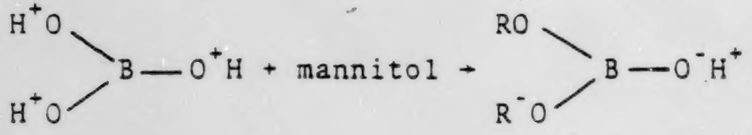
Ryan, L.F. "The Impact of Powdered Ion-Exchange Resins for Water Treatment on BWR Operations." Proceedings of the American Power Conference, No. 35. 1973.

APPENDIX

DERIVATION OF CONVERSION FACTOR

The number 61,830, given on page 28 of this module, is a constant to convert the liquid base volume used to titrate the boric acid solution (part of the reactor primary) into ppm of boric acid. The reasoning behind this particular value is as follows (please refer to formula at bottom of page 28):

1. The ml base x normality of base = milliequivalents of base (meq).
2. Each meq of base = one meq of boric acid.
3. One meq of boric acid weighs 61.83 milligrams (by definition) when used with mannitol, which chemically disables (or ties up) two of the three hydrogens as shown below:



3 hydrogen to titrate 1 hydrogen to titrate

4. The ml base x normality of base x 61.83 = milligrams of boric acid in ml (of sample taken).
5. Number of grams of sample taken is almost exactly equal to number of ml of sample taken because boric acid solution density is about 1 gram/ml.
6. The ml base x N x 61.83/ml sample ≈ mg boric acid/gram of sample.
7. To convert mg/gram to ppm: divide by 1000 to convert mg of boric acid to grams boric acid, then multiply by 1 million to convert this expression from gram/boric acid/gram sample to ppm. That is, the expression in

No. 6 above must be multiplied by 1000 to give ppm. The final expression, therefore, includes a number: 61.83 x 1000 = 61,830.

1. Define:

   Continuous monitoring.

   Grab sample.

   Gravimetric analysis.

   Colorimetric analysis.

   Flame-emission analysis.

   Radiochemical analysis.

2. Briefly describe major chemical sampling techniques used at nuclear power plants:

3. Briefly describe general principles of these chemical analysis systems:
   - Gravimetric.
   - Colorimetric.
   - Volumetric.
   - Flame.
   - Radiochemical.

4. List reasons for collecting and analyzing chemical and radiochemical samples under the following conditions:
   - Power operation.

Subcritical operation.

Refueling operation.

5. List reasons for collecting and analyzing chemical and radiochemical samples from the following:
   Purification system.

   Steam generator system.

   Reactor coolant system.

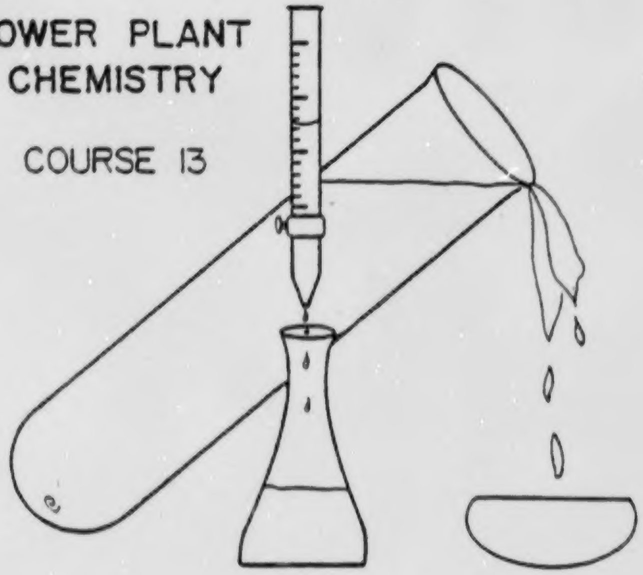
NUCLEAR TECHNOLOGY

MODULE 13-7 RADIOACTIVE WASTE HANDLING - LIQUID AND GASEOUS. -

ROBERT B. NEEL

POWER PLANT
CHEMISTRY

COURSE 13



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COURSE MODULES

COURSE 13 POWER PLANT CHEMISTRY

MODULE 13-1	Water Quality Control
MODULE 13-2	Raw-Water Treatment
MODULE 13-3	Sources of Impurities in Reactor Water Systems
MODULE 13-4	Water Treatment - Polishing by Ion Exchange, Evaportation and Demineralization
MODULE 13-5	Water Properties Sensing
MODULE 13-6	Water Analysis for Nuclear Power Plants
⇨ MODULE 13-7	Radioactive Waste Handling - Liquid and Gaseous

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INTRODUCTION

Electrical production from nuclear energy is among the cleanest (least polluting) forms of large-scale energy production; however, it does discharge very small (but measurable) quantities of radioactive liquids and gases to the environment. These limited emissions are carefully governed by codes (criteria) established by the Nuclear Regulatory Commission, the Environmental Protection Agency and by the States. This module acquaints the student with 1) types and quantities of nuclear wastes generated (under normal reactor operating conditions), 2) the codes that govern these discharges and 3) the current methods for controlling effluent radioactivity.

MODULE PREREQUISITES

The student should have successfully completed all previous Modules in this Course.

OBJECTIVES

Upon completion of this module, the student should be able to:

1. List major sources of gaseous waste in nuclear power reactors.
2. List major nuclides (and their origins) in gaseous waste.
3. Briefly explain how a large-volume pipe in a BWR gaseous-waste disposal system helps to limit radioactivity in effluent.
4. Briefly explain high-efficiency filter use in the gaseous-effluent pipes of a BWR and, after the decay tanks, in a PWR.
5. List differences between PWR and BWR gaseous-waste treatment systems.,
6. List major radionuclides in liquid waste.
7. List major sources of liquid waste (PWR and BWR).
8. Describe treatment methods normally used for radionuclides in power plant liquid effluents:
    - Ion exchange.
    - Evaporation.
    - Filtration.
9. Discuss when demineralization is used in liquid-waste treatment systems.
10. List major differences between PWR and BWR liquid-waste treatment systems.
11. Discuss pertinent sections of 10CFR20 and 10CFR50, which relate to liquid- and gaseous-waste disposal procedures and systems.

SOURCES OF GASEOUS WASTE IN POWER PLANT REACTORS

Radionuclides in gaseous wastes originate from four major sources common to both PWR's and BWR's.

Activation of deuterium and oxygen isotopes in coolant water.

Activation of argon gas dissolved in coolant (caused by air in-leakage).

Fission product gases that leak from cracks in defective fuel elements.

Gas from fission of "tramp" uranium on fuel pellets.

WASTE GASES FROM NEUTRON ACTIVATION

When coolant water passes through a reactor core, the high thermal neutron flux reacts with various naturally occurring isotopes of oxygen in the water molecules. The most abundant isotope is ^{16}O (99.76%). Its reaction with neutrons produces radioactive nitrogen gas:

$$ {}^{16}_{8}O + {}^{1}_{0}n \rightarrow {}^{16}_{7}N + {}^{1}_{1}H $$

$$ {}^{16}_{7}N + {}^{16}_{7}N \rightarrow {}^{16}_{7}N_{2} \uparrow. $$

Equation 13-7-1
(Equation = Eq.)

A small amount of ^{16}O reacts with the produced protons (${}^{1}_{1}H$) to generate radioactive $^{13}N_2$ gas in a two-step nuclear reaction:

$$ {}^{16}_{8}O + {}^{1}_{1}H \rightarrow {}^{17}_{7}F $$

$$ {}^{17}_{9}F \rightarrow {}^{4}_{2}He + {}^{13}_{7}N $$

$$ {}^{13}_{7}N + {}^{13}_{7}N \rightarrow {}^{13}_{7}N_{2} \uparrow . \qquad \text{Eq. 13-7-2} $$

The half-life of ${}^{16}N$ is about 7 seconds, and ${}^{13}N$ is about 10 minutes; thus, during its passage to the gas disposal stack, ${}^{16}N_2$ decays completely, leaving a small quantity of ${}^{13}N_2$ gas. (${}^{13}N_2$ release rate is about 400 μCi/sec).

Argon gas, dissolved in the primary coolant (up to 1 volume percent), forms radioactive ${}^{41}Ar$. Dissolved argon gas originates from air, which leaks into the cooling system. Deuterium (${}^{2}H$), an isotope of hydrogen found naturally in water to 200 ppm, reacts with thermal neutrons to form tritium ${}^{3}_{1}H$, ultimately producing tritated water (half-life of 12.3 years):

$$ {}^{2}_{1}H + {}^{1}_{0}n \rightarrow {}^{3}_{1}H + \gamma . \qquad \text{Eq. 13-7-3} $$

The "chemical shim" in a PWR, which contains boron, also forms tritium from reactions with thermal neutrons:

$$ {}^{10}_{5}B + {}^{1}_{0}n \rightarrow {}^{3}_{1}H + 2\,{}^{4}_{2}He . \qquad \text{Eq. 13-7-4} $$

WASTE GASES FROM FISSION PROCESS

Major radionuclides from this source are caused by leakage from defective fuel elements or by "tramp" uranium (Table 13-7-1). All releases of fission gas are primarily

TABLE 13-7-1

ESTIMATED GASEOUS EFFLUENT ACTIVITY FROM 1000 MWe LIGHT-WATER REACTORS

		Release Rate (microcuries*/sec)1/		
	Half-Life	30 min delay 2/	1 day delay 3/	60 day delay 4/
^{83m}Kr	1.86 hr	3,600	0.5	0
^{85}Kr	10.76 yr	10	10	10
^{85m}Kr	4.4 hr	6,400	156	0
^{87}Kr	1.3 hr	19,200	0.06	0
^{88}Kr	2.8 hr	20,400	60	0
^{89}Kr	3.2 min	440	0	0
Total Kr activity (microcuries/sec)		50,000(approx)	226	10
			15 day delay 3/	
^{131m}Xe	11.9 day	15	6	0.4
^{133}Xe	5.27 day	6,400	880	2
^{133m}Xe	2.3 day	240	2	0
^{135}Xe	9.2 hr	21,600	0	0
^{135m}Xe	15.6 min	10,400	0	0
^{137}Xe	3.8 min	1.120	0	0
^{138}Xe	14 min	31,200	0	0
Total Xe activity		72,000(approx)	888	2.4
Total Xe and Kr Activity (microcuries/sec)		122,000	1,100	12
Total Xe and Kr Activity (curies/yr)		3,000,000	27,500	300

1/ Assumes operation with 0.2% clad defects.

2/ Typical hold-up time in BWR's built to date.

3/ Typical hold-up times for BWR's using charcoal beds.

4/ Typical hold-up time in PWR's.

* Microcurie = 10^{-6} curie = 0.000001 curie.

composed of radioisotopes of xenon or krypton. The quantity of fission gas present depends upon the gas mixture's age.

Waste treatment systems (for BWR's) were originally designed to release gas as waste effluent after a 30-minute delay; current BWR plants are designed with up to a 15-day delay before effluent release. The difference in effluent activity is striking. PWR systems still use a 60-day delay, with significantly lesser concentration of waste fission gas in the effluent.

The compositions of radioactive waste gases for various types of reactors for variable times of release are given in Table 13-7-2. Notice that, with increasing gas-retention time, the waste gas activity decreases from about 122,000 µCi/sec to 12 µCi/sec because nuclides with short half-lives have had sufficient time to undergo decay.

TABLE 13-7-2
GAS EFFLUENT RELEASE DATA

Reactor Type	Gas-Retention Time		
	30 min	15 days	60 days
"Old" BWR	$^{13}N_2$, ^{41}Ar, $^{3}H_2$, Xe, Kr	-	-
"New" BWR	-	Xe, Kr, $^{3}H_2$	-
PWR	-	-	Xe, Kr

BWR GASEOUS-WASTE TREATMENT SYSTEMS

Gaseous waste originates at three major points in a BWR:

Noncondensable gases from main condenser.
Turbine gland seals.
From process systems (laboratories, etc).

GASEOUS WASTE TREATMENT IN "OLD"-DESIGN BWR

More than 99% of all gaseous radioactivity from a BWR is contained within gases originating in reactor coolant water. Gases released by steam-operated air ejectors pass from condenser to ≈150 feet of a 36-inch (0.92 meter) diameter pipe (Figure 13-7-1), which increases the time it takes

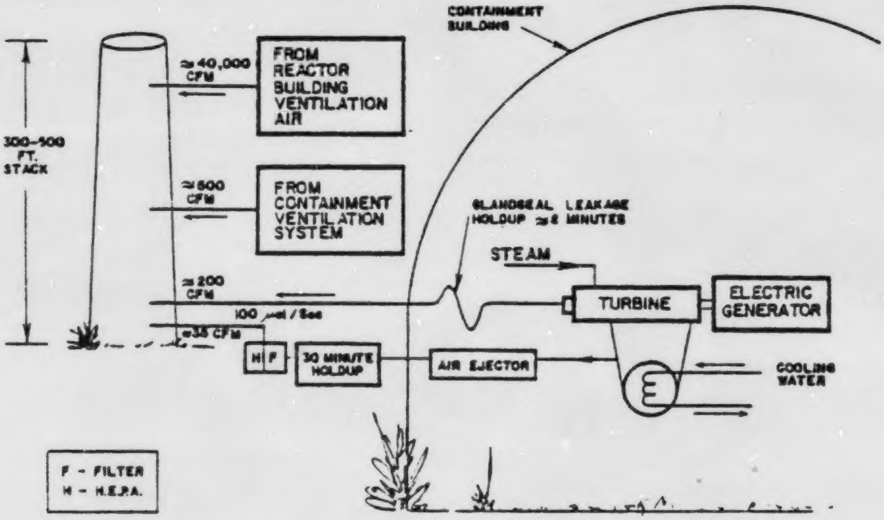

Figure 13-7-1. Early BWR gaseous-waste system.

for a slug of waste gas to reach the stack outlet by ~30 minutes.

During this 30-minute delay, many short-lived radionuclides (e.g., $^{16}N_2$) decay away, reducing the concentration of radioactive waste gas before it enters the atmosphere. The radionuclides also decay during their movement from the elevated point of release at the stack (300 to 500 feet) to ground level. (Each plant must determine this release time from meteorological data taken at or near the site of the reactor.)

Only about 0.1% of the radioactivity boiled out of the water in the core is vented through the turbine gland seal. An enlarged pipe provides several minutes of holdup time for the released gas. During this time, $^{16}N_2$ and $^{19}O_2$ decay completely. Small residual quantities of krypton and xenon gases become so diluted by containment and ventilation air that they present a very small radiation hazard at the release point (compared with waste gases from condenser air ejectors).

GASEOUS WATER TREATMENT IN CURRENT-DESIGN BWR

To meet tighter Government standards for off-site radiation exposure, General Electric Company, as an example, modified its gaseous-waste system (Figure 13-7-2).

The relative volume of radioactive gases is insignificant compared with the volumes of air, hydrogen and oxygen removed from the main condenser by condenser air-ejectors. Dilution of hydrogen gas, to below the lower exposure limit (4.1% by volume in air), by steam in the air-ejectors may not always occur. The catalytic recombiners promote the

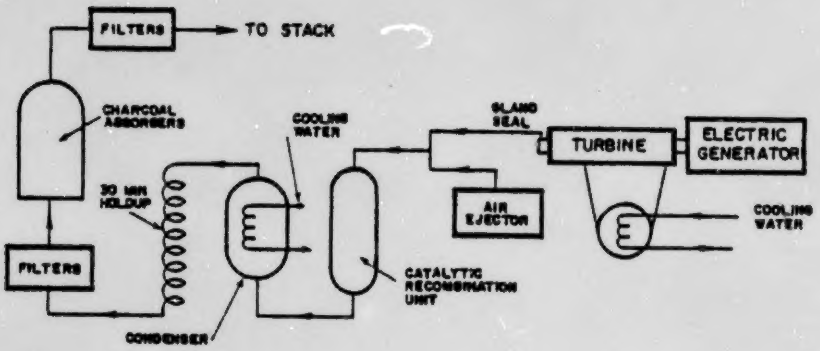

Figure 13-7-2. Improved BWR off-gas system.

reaction of hydrogen, in a controlled way, with oxygen (in air) to produce water vapor. Tritium, an isotope of hydrogen, is also removed by the catalytic recombiners. After cooling the resulting gas to 130°F (55°C) to condense out water vapor, the resulting volume is about 10% of its initial value. A 30-minute holdup removes most other radioactive gases with short half-lives.

The remainder of an improved BWR off-gas system is designed to remove particles and isotopes of krypton and xenon. Airborne radioactive particulates are removed by a high-efficiency particulate air (HEPA)-charcoal filter combination. HEPA filter units are assembled into modules with cross sections of up to 24 inches x 24 inches and depths of up to 11-1/2 inches (Figure 13-7-3). From an end view, the filter medium (a pleated mat of woven fireproof fiberglass) and filter separators are both visible. New HEPA filters must have efficiencies of 99.97% when tested with uniformly sized particles of 0.3-micrometer

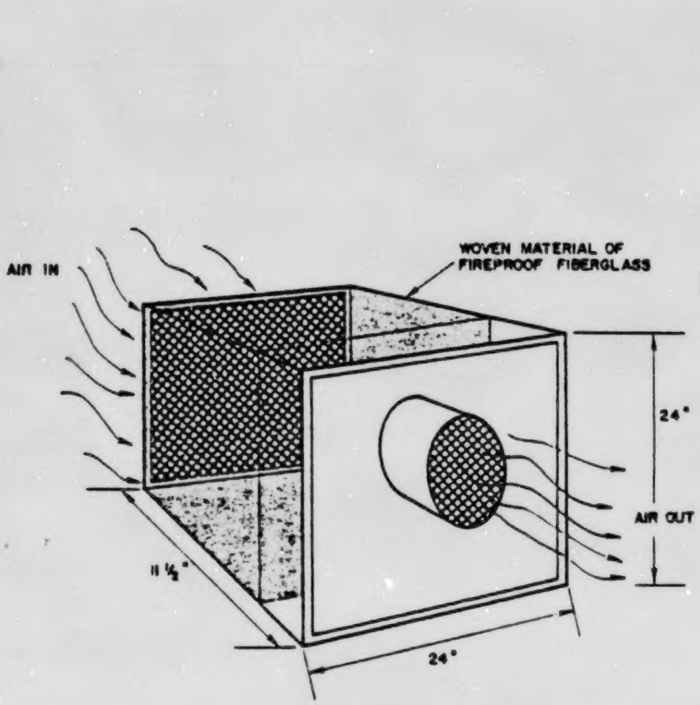

Figure 13-7-3.
Nuclear grade separator-type HEPA filters.

diameter (about 12 millionths of an inch). In-place testing of each HEPA filter system is required to establish that only negligible leakage of air occurs around the gaskets in the filter housing. To prevent large particles from blinding (plugging) pores of the filter, a prefilter is almost always used.

The charcoal bed delays passage of isotopes (both xenon and krypton) before release to the atmosphere. Duration of delay depends upon bed length (for any given bed diameter). With no air in-leakage and with a gas flow of 30 ft^3/min through the bed from the main condenser, charcoal holds krypton isotopes for about 24 hours and xenon isotopes for up to 15 days.

Although very little iodine is present in the off-gas during normal operation, charcoal can retain over 90% of it, even in the event of an LOCA (loss-of-coolant accident).

The last filter, after the charcoal beds, prevents fine particles of charcoal from passing to the stack. Current systems are roughly 1000 times more effective than older systems in reducing off-site exposure when used with a 350-foot stack.

PWR GASEOUS-WASTE TREATMENT SYSTEMS

In a PWR, most radioactivity is carried off by liquid effluent. Ventilation air, containment air and condenser air-ejectors contain negligible gaseous radioactivity; however, three major points of origin for gaseous waste do exist:

De-gassing of primary coolant.
Vents for tanks and other equipment containing high-activity liquids.
Vents for tanks containing low-activity liquids.

Gas with high radioactivity and high hydrogen content originates from the surge tank in the chemical and volume control system (CVCS) of a PWR (Figure 13-7-4). This tank is the one into which chemicals are added and mixed with primary water. During mixing, some out-gassing of primary coolant occurs; this gas is vented to the suction inlet of two surge gas compressors. The gases are compressed into the surge tank and then processed through a hydrogen/ oxygen recombiner system (not shown in Figure 13-7-4) to reduce hydrogen concentration by conversion to water vapor.

In some PWR waste gas systems, no recombiner is included, but nitrogen is continuously bled into the system to reduce hydrogen content to below 4.1 percent of volume, its lower

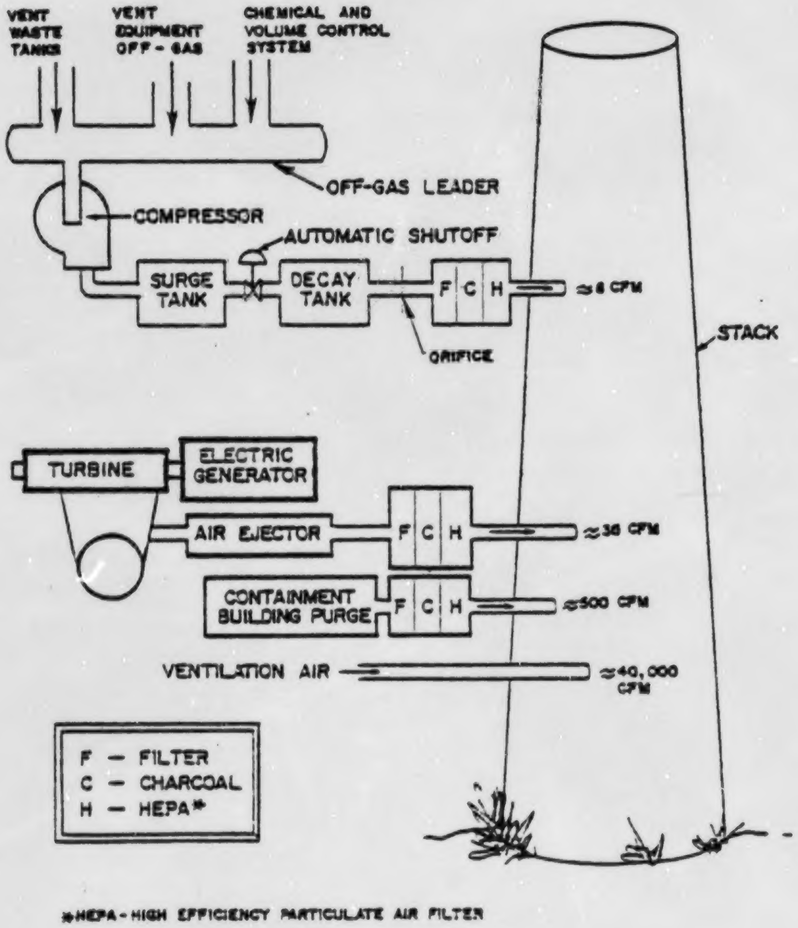

Figure 13-7-4. PWR gaseous waste system.

explosive limit. Gases in the three decay tanks are at about 100 psig, where they are held for storage (up to about 120 days) to allow decay of isotopes of iodine, krypton and xenon.

When activity in the tanks is known to be below allowable discharge levels for plant site, gases are bled at a controlled rate through waste-gas filters to the stack. The orifice (Figure 13-7-4) measures flow rate of released gases; the filter is a HEPA-charcoal combination (as was described for BWR). When discharged gas activity exceeds the control point of a continuous radiation monitoring system, an outlet valve on the tank closes automatically.

A low-activity waste gas system contains mainly air (contaminated with small amounts of activity and hydrogen) vented from waste storage tanks and equipment. The chemical drain tank, laundry drain tank and low-activity liquid waste holdup tanks are typical sources of this kind of gaseous waste. The waste is processed in a manner identical to the high-activity gaseous waste described above.

A third type of gas stored in gas decay tanks originates from liquid sources containing large amounts of radioactivity but low concentrations of hydrogen. When waste gas pressure increases to a preset value, the compressor automatically transfers excess gases to a decay tank. The most significant sources of off-gas activity, in this class, include waste storage tanks and evaporators [for example, spent-resin storage tank, reactor coolant evaporators, waste evaporator concentrate (bottoms) storage tank, and tritated waste holdup tank].

RADIONUCLIDES IN LIQUID WASTE FROM POWER REACTORS

Radionuclides present in liquid waste solutions consist of 1) dissolved xenon, krypton and iodine gases, 2) dissolved and suspended fission products from fuel clad leaks and 3) corrosion products.

Soluble and insoluble radioisotopes of iodine, cesium, strontium, yttrium, barium and lanthanum originate as fission products. Other significant radioisotopes of cobalt, manganese, iron, chromium and tritium are generated primarily as corrosion products. These products become radioactive by neutron bombardment during their passage in the vicinity of the reactor core.

Two processes are generally used to treat liquid radwastes:

Evaporation.
Demineralization.

Demineralization is only used when total solids content of effluent liquid is low. If dissolved solids content is high, resins are exhausted rapidly because of the limited number of ion-exchange sites. What is done normally is to use evaporation to boil off relatively pure water, which is very low in dissolved solids content. Relatively pure distillate is condensed and finally passed through a demineralizer to remove traces of dissolved solids.

Filtration systems used in liquid waste treatment are usually cartridge or pre-coat filters. These filters often precede ion-exchanger beds or evaporators to remove substantial amounts of insoluble solid corrosion products. This arrangement prevents clogging of resin-bed pores and it minimizes deposition of solids on heat-exchanger tubes (of the evaporators), which results in reduced heat transfer.

PWR LIQUID WASTE TREATMENT SYSTEM

Routinely generated high-activity liquid wastes from a PWR contain several $\mu Ci/cm^3$ of activity arising from the following processes:

Leakage by primary system equipment (pumps, etc.).

Solutions from laboratory samples of primary system drained to waste.

Solutions from dilution of reactor coolant water during changes in reactivity initiated by changes in concentration of boric acid (chemical shim).

Other high-activity wastes are generated only at specific times, for example, during regeneration of demineralizer resins or during startup - i.e., overflow when coolant expands (Figure 13-7-5).

Low-activity waste solutions, which contain a fraction of a $\mu Ci/cm^3$, include:

Solutions drained from floors of reactor or auxiliary buildings.

Dirty solutions from hot shower room and laundry room equipment.

Corrosive solutions from laboratory and from equipment decontamination.

Blowdown from steam generator, which may contain some activity if leaks occur at tubes separating primary from secondary system.

In a PWR, liquid wastes are collected in separate tanks and, when ready for processing, are pooled into a single waste holdup tank. Waste, in this tank, is chemically sampled to determine types of chemical addition, if any, that must be made to facilitate evaporation. When dissolved

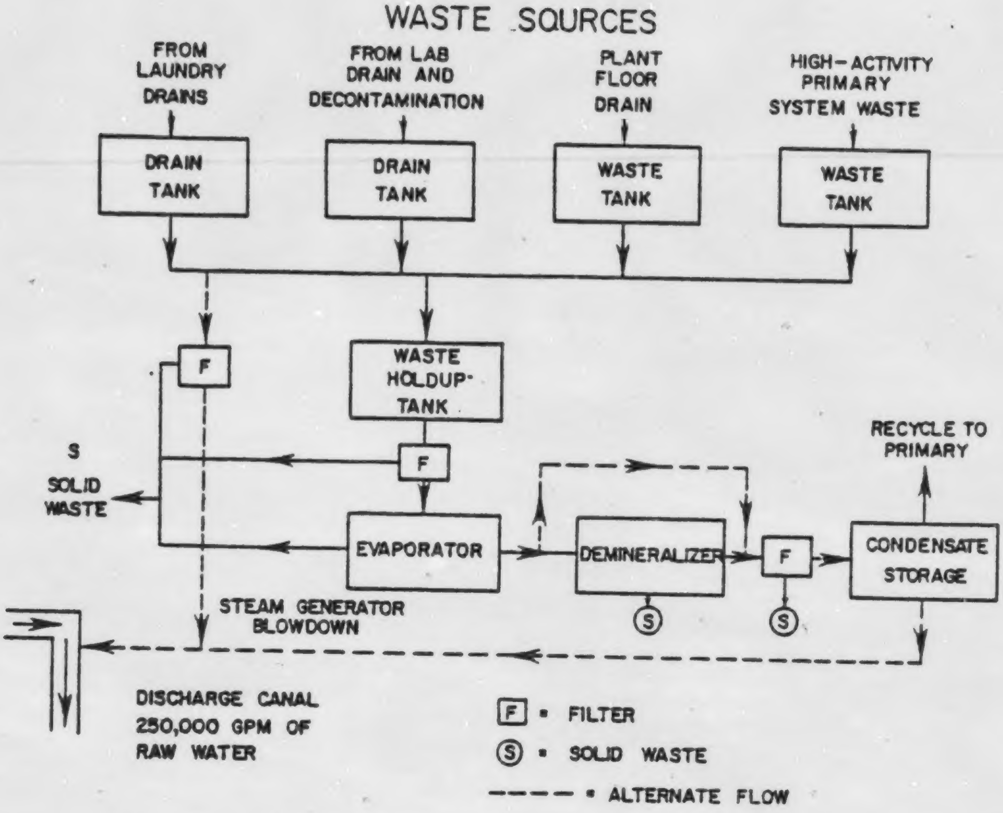

Figure 13-7-5. PWR liquid waste system.

radioactivity greatly exceeds concentration allowed for effluent discharge, or if the total solids content of waste is high, waste is pumped from waste holdup tank into evaporator. Decontaminated distillate, after being condensed, is further processed through a demineralizer to remove traces of activity carried over from evaporator. After filtration, this "clean" solution may be stored in condensate storage tank for recycling (as reactor makeup water) or pumped into a discharge canal for release. Bottoms, from evaporator, which contain a concentrated solution of radioactivity, are solidified into concrete and disposed of as solid radwaste. Filters in this system, disposable cartridges, are also disposed of as solid radwaste.

If radioactivity content is small enough, filtration of waste solutions, followed by dilution in discharge canal, may be adequate treatment.

Blowdown, from secondary system of a PWR, frequently contains small amounts of radioactivity because of leakage (from primary to secondary system) of corrosion off the heat-exchanger tubes. Blowdown can be pumped directly to demineralizers for decontamination. After cleanup, solution may be stored for recycle into reactor system, or diluted with liquid (in the discharge canal) for release.

BWR LIQUID WASTE TREATMENT SYSTEM

BWR waste solutions are collected and sorted into special groups, based on electrical conductivity of waste solutions as well as radioactivity content. There are four classes of such liquid waste (Figure 13-7-6).

The first source includes liquids with conductivities of less than 50 μmhos/cm - high-purity waste solutions. They result largely from regeneration of deep-bed condensate demineralizers and from decontamination of piping and equipment in primary coolant systems. These solutions are filtered, demineralized to remove traces of radioactivity and pumped into storage tanks for later use as reactor makeup water or for release to a discharge canal.

Waste solutions, with conductivities of between 50 and 100 μmhos/cm, may originate from reactor building and turbine building floor drains, from water used to sluice resins

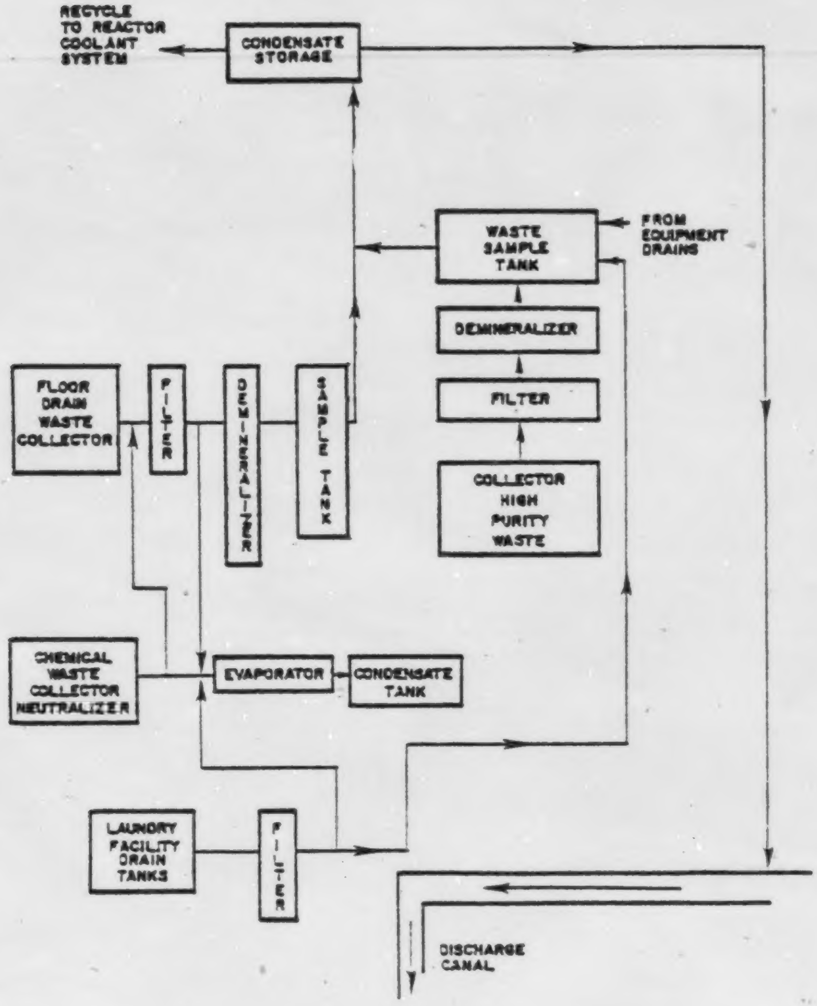
RECYCLE TO REACTOR COOLANT SYSTEM
CONDENSATE STORAGE
WASTE SAMPLE TANK
FROM EQUIPMENT DRAINS
DEMINERALIZER
FILTER
COLLECTOR HIGH PURITY WASTE
FLOOR DRAIN WASTE COLLECTOR
FILTER
DEMINERALIZER
SAMPLE TANK
CHEMICAL WASTE COLLECTOR NEUTRALIZER
EVAPORATOR
CONDENSATE TANK
LAUNDRY FACILITY DRAIN TANKS
FILTER
DISCHARGE CANAL

Figure 13-7-6. BWR liquid waste system.

to and from regeneration tanks and from evaporator condensates. These liquids are collected, filtered, demineralized and stored (if conductivity is less than 50 μmhos/cm) or released to a discharge canal (if concentration of radioactivity is less than legal limits after dilution with raw water from discharge canal).

Wastes with high conductivity are collected in a neutralizer tank for chemical modification. These wastes include laboratory and laundry wastes with higher total solids content. If radioactivity is low enough to meet legal standards after dilution with water in a discharge canal, pH is adjusted to a pH of from 7 to 10 (by adding caustic solution) and the liquids are released to a canal without further treatment.

If radioactivity is too high for this type of discharge, the wastes are concentrated in an evaporator. The bottoms are pumped to a waste storage tank for future solidification with cement into solid radwaste.

Distilled liquid is collected in a condensate tank for further purification by demineralization before recycling to the reactor water makeup system.

REGULATORY REQUIREMENTS FOR DISPOSAL OF LIQUID OR GASEOUS WASTE

All disposal of radioactive gases, liquids and solids at a nuclear power plant is regulated primarily by two Federal documents (issued by the Nuclear Regulatory Commission): Title 10, Code of Federal Regulations, Part 50, "Licensing of Production and Utilization Facilities," and Part 20, "Standards for Protection Against Radiation." These codes are usually abbreviated to 10CFR50 and 10CFR20.

Illustrations of acceptable waste treatment and disposal performance in accordance with these codes are periodically issued as Regulatory Guides by the Commission. Some states have reached agreement with the Commission on standards and methods of enforcement of these laws; in these states, called "agreement" states, enforcement and surveillance are normally carried out by state officials rather than by agents of the Federal Government.

TITLE 10, CODE OF FEDERAL REGULATIONS, PART 50, "LICENSING OF PRODUCTION AND UTILIZATION FACILITIES," (10CFR50)

This regulation requires an owner to file for a permit from the Commission to construct a nuclear facility. Another permit is required for operation of the plant. Also, a preliminary safety analysis report (PSAR) must be submitted to the Commission, in which the design of processes and equipment for control of releases of any radioactivity is clearly specified. Also required is a lengthy review of the technical details of how the owner intends to protect the environment (including people). This PSAR is reviewed by Government engineers and then subjected to a public hearing.

The owner incorporates suggestions of both public and Government advisors into a final safety report (FSR). If this report is accepted, the Commission issues "Technical Specifications" for that particular reactor. These specifications define operational limits on temperature, pressure, flow, concentrations and quantities of gaseous and liquid effluents that may be discharged from the reactor waste system.

In 1976, 10CFR50 was amended to include an Appendix I, which made mandatory that all releases of radioactive effluents from nuclear power plant waste systems be "as low as practicable." Guidelines on how low off-site exposure should be were based on the state of the art of waste disposal treatment and control technology at the time the law was drafted. The regulation may be paraphrased as follows:

Liquid waste disposal - No individual in an unrestricted area (beyond the control of the company) may receive (from all exposure pathways) more than 3 millirems/year to total body, or more than 10 millirems/year to any single organ.

Gaseous waste disposal - No more radioactivity may be released than will give an individual (on the site boundary continuously) more than 5 millirems/year total body dose, or more than 15 millirems/year to any single body organ.

Exposure to a hypothetical individual who spends 365 days a year on the site boundary (three shifts a day) is inferred from instrumental measurements. The owner must maintain documented records of all monitoring activities for many years into the future. Penalties may be levied for failure to keep proper radiation monitoring facilities or records as required by this Code.

TITLE 10, CODE OF FEDERAL REGULATIONS, PART 20, "STANDARDS FOR PROTECTION AGAINST RADIATION," (10CFR20)

Section 20.106 defines the point of release of a gaseous or liquid effluent as that point from which radioactivity leaves a pipe or stack.

Other sections of 10CFR20 effectively limit burial of solid wastes on reactor sites, and the incineration of combustible liquids or solids that contain radioactivity.

Moreover, several sections of the Code require that "instantaneous concentration" of any radionuclide in a waste effluent must be less than the "legal concentrations" given in the Code's Appendix B, Table II (for unrestricted areas).

Other tables in the Code refer to permissible concentrations for occupationally exposed workers on the reactor site.

Federal laws require the employer to report to employees (and guests) radiation exposure accumulated during any quarter year of work and during any year of work. If these guidelines for exposure are exceeded, special reports, which explain how and why radiation standards were violated, must be submitted in writing to the Commission or agreement state regulatory agency. Individual records of radiation exposure must be maintained for each employee.

These brief comments on Federal codes only introduce the subject to the serious student. A review of Code documents and their extended use in day to day operations is necessary to actually master them and their interpretations.

EXERCISES

1. How many pounds of deuterium oxide are in 100,000 gallons of normal reactor cooling water? (Assume density of water is 44 lb/ft^3 at 580°F, PWR operational temperature.)
2. Assume that 1% of this D_2O is converted to tritium oxide. How many pounds of tritium oxide are formed?
3. If the temperature of cooling water (inside the con-

denser in Figure 13-7-2) is 20°F too high, would retention time of xenon (or krypton) on the charcoal absorbers increase or decrease? Why?

4. Why is air from the ventilation system of a PWR (or a BWR) always connected to the stack that vents radioactive gas?
5. If a chemical lab technician accidentally spills one pint of concentrated sulfuric acid in a laboratory sink, where would it be expected to go in the waste system in a PWR (and in a BWR)?
6. If a liquid waste evaporator breaks down, can a utility operator dispose of a solution containing:
   High-radioactivity, high-solids content?
   High-radioactivity, low-solids content?
   Give reasons why disposal within the legal discharge limits (is or is not) possible.

MATERIALS

None.

PROCEDURES

Obtain a copy of the Code of Federal Regulations, Title 10, Energy, Parts 20 and 50.

1. In Part 20, look up the following definitions and write down their meanings:
    - Act.
    - Airborne radioactive material.
    - By-product material.
    - Occupational dose.
    - Person.
    - Radiation.
    - Radioactive material.
    - Source material.
2. Read Section 20.304, "Disposal by Burial in Soil," and list how you would bury 12 radioactive sources in any one year.
3. Read Section 20.401, "Record of Surveys, Radiation Monitoring and Disposal," and list the form(s) on which records are required to be kept and describe personnel monitoring requirements.
4. In Part 50, look up the following definitions and write down their meanings:
    - Production facility.
    - Utilization facility.
    - Nuclear reactor.
    - Testing facility.
    - Design bases.
5. From Part 50, what is the difference between a Class 104 and a Class 103 license?
6. List, from 50.34a, information to be included (concerning design objectives for equipment) to control release

of radioactive material in effluents.

7. List and describe, from Appendix J, three types of leakage tests required for primary reactor containment structure or vessel.

DATA TABLE

None.

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NRC documents are available by writing the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

TEST

1. List and briefly explain major sources of gaseous waste in a nuclear power reactor:

2. List five major nuclides in gaseous waste; give their origins:

   (1)

   (2)

   (3)

   (4)

   (5)

3. Briefly describe how large-volume pipe (in a BWR gaseous waste disposal system) helps control radioactivity of effluent:

4. Briefly explain uses of high-efficiency filters in gaseous effluent pipe in a BWR and, after the decay tanks, in a PWR:

5. Briefly describe differences between PWR and BWR gaseous waste treatment systems:

6. List major nuclides in liquid waste; give source of each:

7. List and briefly describe treatments for radioactive nuclides in nuclear power plant liquid effluent:

8. Briefly note instances when demineralization is used in liquid waste treatment:

9. Briefly describe differences between PWR and BWR liquid waste treatment systems:

10. Discuss contents of 10CFR20 and 10CFR50 as they relate to gaseous- and liquid-waste disposal procedures and systems:

NUCLEAR TECHNOLOGY

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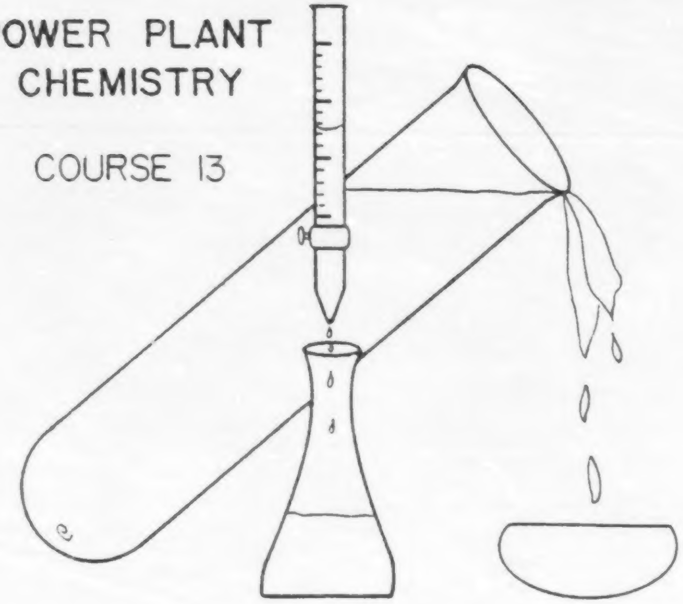

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NUCLEAR TECHNOLOGY SERIES
INDEX
for
COURSE 13, POWER PLANT CHEMISTRY (SEVEN MODULES)

NOTE: Each module in this Course is numbered separately, and the page numbers begin with page 1 in each module. Therefore, this Index lists for each entry the module number (underlined), followed by a comma and the page number. Figures and tables are listed by their numbers, followed by the module and page number in parentheses. A Master Index is available in a separate volume. This general index merges all index entries from the 35 Nuclear Courses. It is a valuable research tool, with which the student or researcher can locate all the references to any subject within the 35 Courses.

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